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LASER WINDOW STUDIES

D. Bua, et al

Raytheon Company

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) <b>This report deals largely with the characterization of films (ZnSe, ZnS, As<sub>2</sub>S<sub>3</sub> and ThF<sub>4</sub>) on high power laser window substrates (BaF<sub>2</sub> and ZnSe). Thus far attenuated total internal reflection spectra have been taken of As<sub>2</sub>S<sub>3</sub> on BaF<sub>2</sub>; and calorimetric measurements for film absorption studies have been developed and applied to As<sub>2</sub>S<sub>3</sub> on BaF<sub>2</sub>. A literature search has been undertaken to determine liquid coolants for high power windows but no promising candidates were found. A literature search of the mechanical, physical and chemical properties of films was made. Adhesion measurements have</b>		

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ABSTRACT (Cont'd.)

begun using pull tests and peeling tests, as well as microhardness measurements using a small diamond indenter in conjunction with the scanning electron beam microscope.

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## PREFACE

This report describes work on laser window technology performed during the period from May 20, 1974 to November 20, 1974 on Contract DAAH01-74-C-0719. Participating in the research of this report were J. Grenda, O. Guentert, W. Tye, T. Varitimos, and C. Willingham. This report has an internal number of S-1790.

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## 1. TECHNICAL REPORT SUMMARY

### A. Program Objectives

In recent years laser window technology has developed rapidly to the point where few frontiers remain. The primary candidate materials are well-established. Techniques for hardening the softer materials and fabricating suitably large sizes are already highly developed and optical surface preparation and characterization studies are underway at a number of laboratories.

The one inescapable obstacle which remains to be overcome before the laser window "problem" can be said to be solved lies in the area of coatings and films. In a high power laser system very little back-reflection from the window surfaces can be tolerated; thus, with the exception of those few solutions in which a Brewster angle window is appropriate, the window surfaces will have to be coated for minimum reflection (i.e., AR (anti-reflection) coated).

In addition, because of the hygroscopicity of potassium chloride, protective, "waterproof" coatings are required for physical survival even if a Brewster configuration is possible. Of course, optical coating technology is not new to the laser industry; however, the requirements of the high power laser systems put much more severe restrictions on the characteristics of the films. In particular, the optical absorption must be as low as possible and the mechanical (and hence, thermal) contact to the window substrate as complete as possible.

The primary objective of this research program is to develop new experimental techniques and extend the existing approaches for the characterization of the optical and mechanical properties of the thin films of interest for infrared laser window applications. Additional consideration will be given to further investigation into the nature of the  $10.6\mu\text{m}$  absorption band characteristic of the available potassium chloride materials, a search for low optical absorption liquids for possible use as window coolants and an evaluation of polishing techniques used for the preparation of the barium fluoride ( $\text{BaF}_2$ ) and zinc selenide ( $\text{ZnSe}$ ) windows to be used as substrates for the experimental films.

## B. Major Accomplishments

A literature search on adhesion of thin films to their substrates has been conducted and a literature search for low loss liquid coolants in the 3 - 5  $\mu\text{m}$  and 10.6  $\mu\text{m}$  range has shown that relative spectral windows may exist at the deuterium fluoride, carbon monoxide and carbon dioxide laser frequencies, but the very low losses required for high power window coolants are not reported.

$\text{BaF}_2$  and ZnSe substrate material in the form of ATR (Attenuated Total Reflection)\* plates have been ordered and received. The substrate material has been characterized, with data including micrographs and internal reflection spectra of each ATR plate. Internal reflection spectra have been taken of existing  $\text{BaF}_2$  ATR plates coated on half their surface with arsenic trisulfide ( $\text{As}_2\text{S}_3$ ). Calorimetric measurements were made of the existing  $\text{BaF}_2$  ATR plates, comparing the coated and uncoated sides at both 5.25  $\mu\text{m}$  and 10.6  $\mu\text{m}$ .

The feasibility of coupling polychromatic light into a thin film via prism coupling for the purpose of measuring the absorption coefficient vs wavelength of the film was undertaken and the appropriate apparatus fabricated. Extremely good surfaces are required to couple light into the film. Surface scattering attenuates the light beam and thus only relatively higher absorbing films can be investigated with  $\beta = 1 \text{ cm}^{-1}$  and larger.

Different methods for measuring thin film adhesion were also investigated. We are now testing the direct pull method and the pull tab method. Test jigs have been fabricated to test these approaches. The results of these experiments are reported in the text.

## C. Conclusions

The first half of this contract was spent in ordering appropriate materials and fabricating equipment, and investigating different techniques in the measure-

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\* Attenuated Total Reflection (ATR), discussed later in this report, is reflection which occurs when an absorbing coupling mechanism acts in the process of total internal reflection to make the reflectance less than unity.

ment of optical film parameters. Conclusions derived from these experiments are as follows: The literature search investigation of liquid coolants for high-power laser windows in the infrared identified no promising liquids. Previous experimentation had not been concerned with very low absorption coefficients required for high power windows.

Internal reflection spectroscopy, while a valuable tool in the measurement of spectral absorption in thin films, is not sensitive enough to measure the spectral absorption of low loss films. However, it must still be used in preliminary tests of film absorption because of its convenience in detecting gross absorptions of film impurities.

The integrated optic coupling technique has run into a number of problems associated with the quality of the materials. Further efforts in this area will have to be given serious consideration.

Calorimetry, even though limited to the laser wavelengths, still appears to be the best method of measuring low loss absorbing films. Work with thin substrates will improve the sensitivity of the calorimetric technique. While we will try to improve the other approaches, the calorimetric measurement will be our mainstay in future work.

Adhesion tests on thin films have displayed the same reproducibility problems encountered by other experimenters. It seems that improvement on existing techniques is probably not the answer and that a completely new approach will have to be devised. Initial assessment of the scanning electron beam microscope in conjunction with a fine diamond loading tool shows promise in determining the film hardness.

## II. ACCOMPLISHMENTS AND TECHNICAL DISCUSSION

### A. Literature Search

A series of literature searches were conducted on topics such as techniques for measuring the adhesion of thin films, optical absorption in thin films, and low-loss liquid coolants in the 3 to 5 $\mu$ m and 10.6 $\mu$ m range.

In general, many methods have been devised to measure the adhesion of thin films to substrate material. As many workers in the field have found, reproducibility in the measurements is the problem. Virtually all the physical contact methods to pull the film off the substrate affect the adhesion of the film due to stress and chemical reaction of the adhering epoxy. Interpretation and comparison of other methods can be very difficult.

The important quality that affects the adhesion is the surface energy, i. e., the bonding energy between the substrate and film per unit area. Ideally, this energy can be measured by peeling off the film in a certain way and measuring the required pulling force. However, this method is also fraught with many experimental difficulties. No ideal method has been found.

No new low-loss liquid coolant in the 3 $\mu$ m to 5 $\mu$ m and 10.6 $\mu$ m range have been identified. While there are many liquids which have apparent regions of lower absorption near 3.8 $\mu$ m, 5.3 $\mu$ m, and 10.6 $\mu$ m, no measurements are reported which give absorption coefficient ( $\beta$ ) in the  $10^{-2}\text{cm}^{-1}$  and lower range. Most of these measurements would yet have to be made on the innumerable organic liquids. In general, we do not recommend that such additional measurements be made. All the organic liquids have vibrational frequencies which are comparable to and many times higher than the laser frequencies. We therefore do not have the favorable situation that exists in good laser window crystals where the optical vibrational frequencies are much lower than the contemplated laser frequencies. The results of the literature search on low-loss liquid coolants are in Appendix A.

## B. Materials

### 1. Substrate

Harrick Scientific was selected, on the basis of their experience and past performance, to fabricate the  $\text{BaF}_2$  and  $\text{ZnSe}$  ATR plates. These plates have now been received. The polycrystalline  $\text{ZnSe}$  was grown by Raytheon by chemical vapor deposition (CVD). Only single crystal material of  $\text{BaF}_2$  is presently available. Single crystal samples of  $\text{BaF}_2$  with both (100) and (111) orientation have been obtained.

### 2. Films

Nine suppliers in the infrared optical coating industry were contacted with respect to the deposition of nine different possible thin film materials. Based on these discussions, three well-known suppliers with direct experience in the deposition of the desired materials were selected for the first buy — OCLI, Perkin Elmer and Broomer Research Corporation.

The four materials selected ( $\text{ThF}_4$ ,  $\text{ZnSe}$ ,  $\text{ZnS}$  and  $\text{As}_2\text{S}_3$ ) were chosen because of their currently recognized utility in low-loss, high-power window coatings: Figures 1, 2, 3, and 4 are typical optical transmission curves of the four materials. The bulk values of the absorption coefficient and index of refraction at  $5.25\mu\text{m}$  and  $10.6\mu\text{m}$  for these materials are shown in Table I.  $\text{ThF}_4$  is universally used as the low index material in multilayer coatings;  $\text{ZnSe}$  and  $\text{ZnS}$  are rapidly becoming the "standard" high index materials; while  $\text{As}_2\text{S}_3$  appears to be the leading candidate for the protection of the hygroscopic halide materials. The initial order included two coatings of the  $\text{ThF}_4$ ,  $\text{As}_2\text{S}_3$ , and  $\text{ZnSe}$  on  $\text{BaF}_2$  substrates and two coatings of  $\text{ZnS}$ ,  $\text{ThF}_4$ , and  $\text{As}_2\text{S}_3$  on  $\text{ZnSe}$  substrates from each of the three suppliers — a total of 36 samples in all. Each ATR plate will be coated on only half the surface so that a surface/substrate reference spectrum can be made. A realistic film thickness of  $\lambda/2$  at  $5\mu\text{m}$  has been chosen.

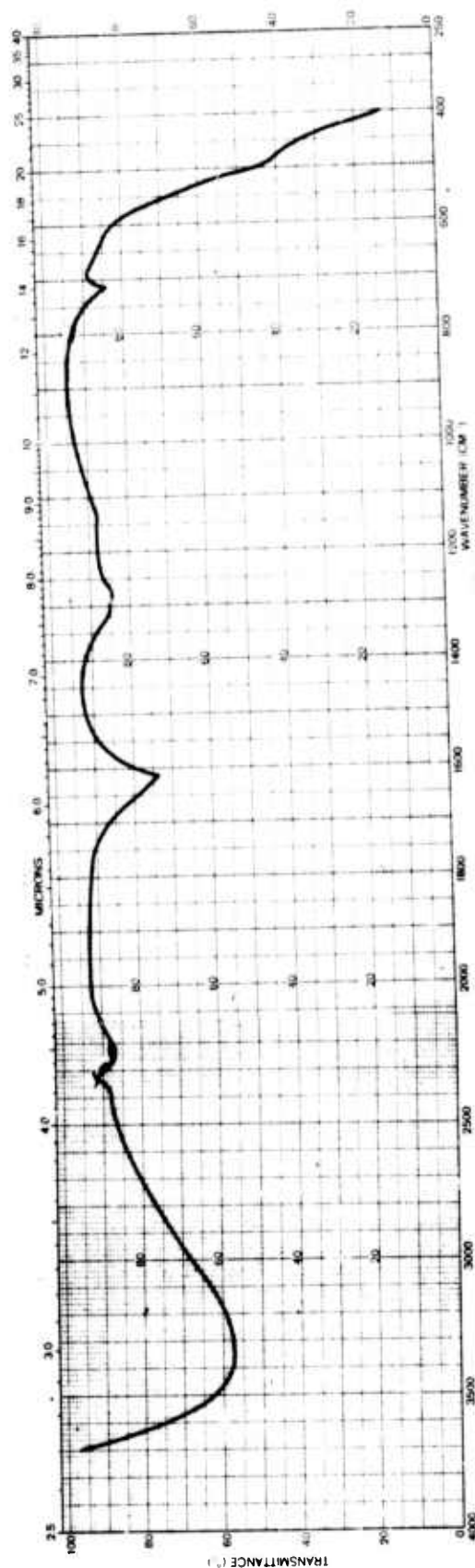


Fig. 1 ThF<sub>4</sub> · 4H<sub>2</sub>O Bulk Spectrum from Infrared Spectra of Inorganic Compounds, R. A. Nyquist and R. O. Kagel.

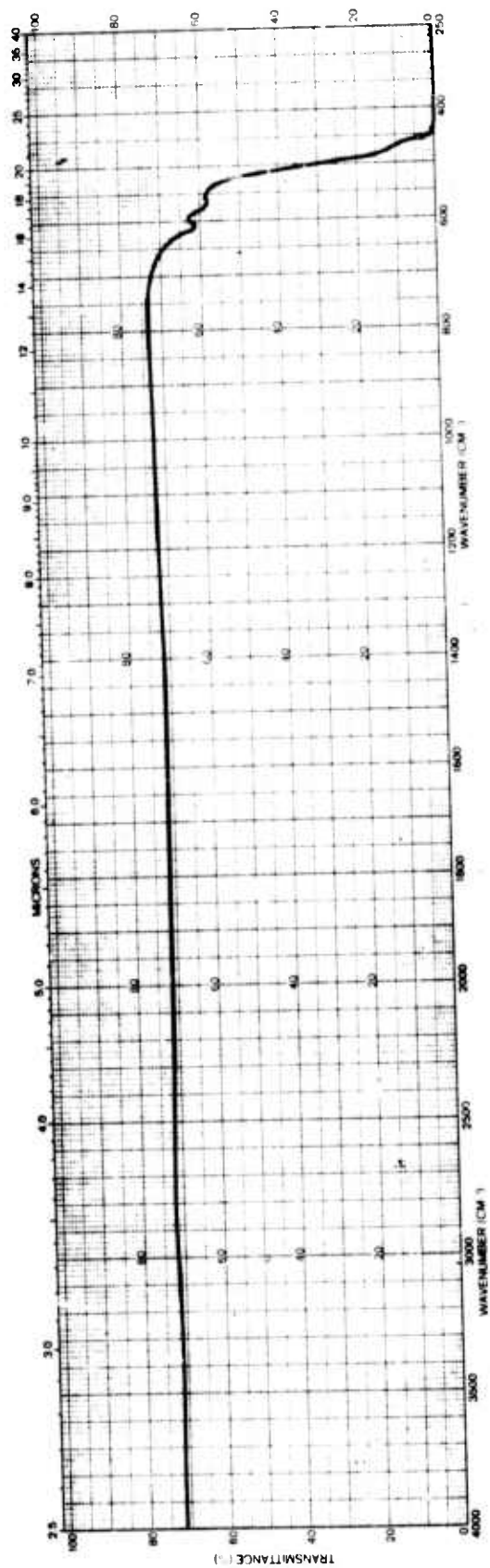


Fig. 2 Zinc Selenide (Grown by Chemical Vapor Deposition), Bulk Spectrum.

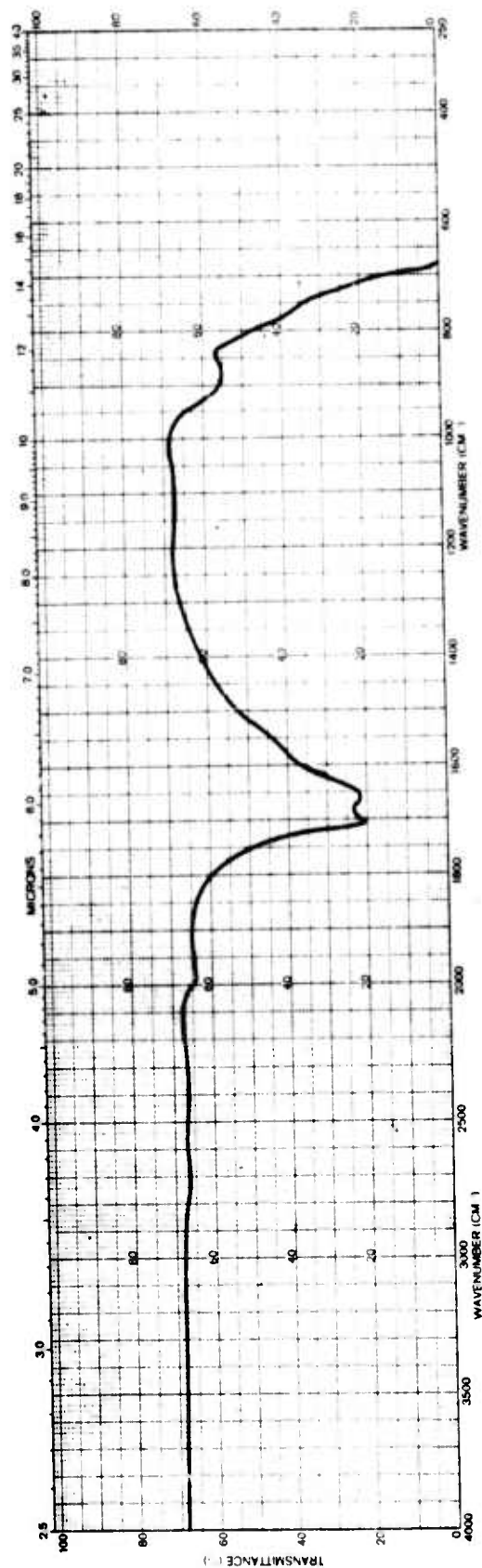


Fig. 3 Zinc Sulfide (Grown by Chemical Vapor Deposition), Bulk Spectrum.



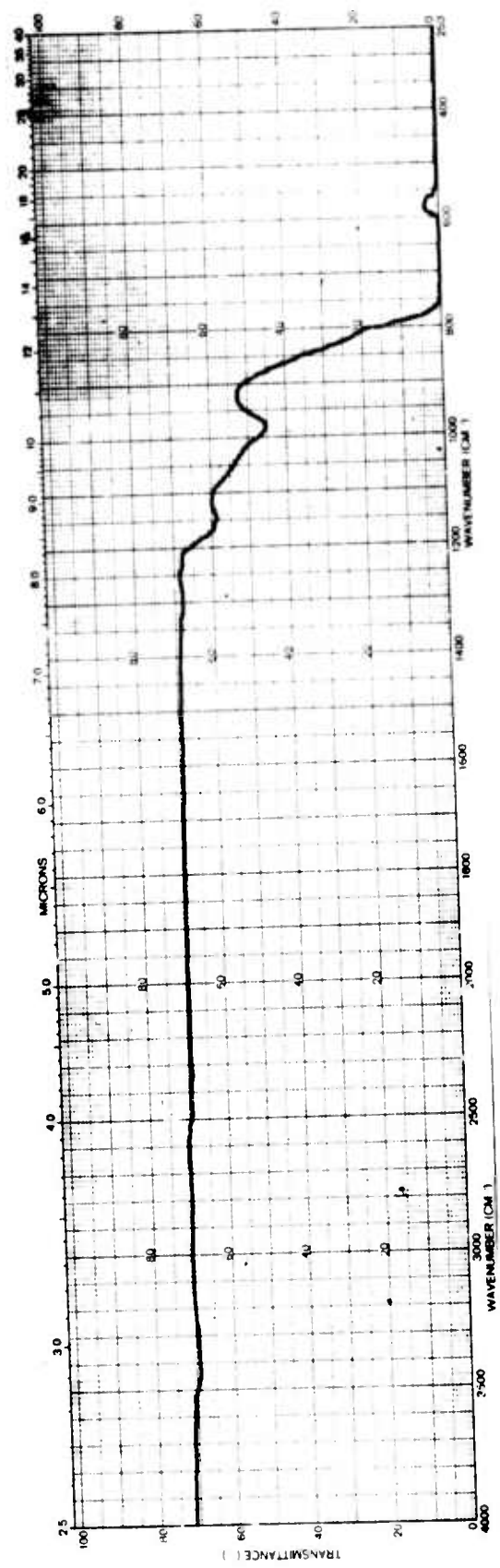


Fig. 4 Arsenic Trisulfide Bulk Spectrum.

TABLE I  
BULK MATERIAL PARAMETERS

	<u><math>10.6\mu\text{m}</math></u>		<u><math>5.25\mu\text{m}</math></u>	
	<u><math>\beta (\text{cm}^{-1})</math></u>	<u><math>n</math></u>	<u><math>\beta (\text{cm}^{-1})</math></u>	<u><math>n</math></u>
* ZnSe	.001 - .005	2.4	$3 \times 10^{-4} - 10^{-3}$	2.42
ZnS	.15	2.217	< 0.1	2.249
ThF <sub>4</sub>		1.5		
As <sub>2</sub> S <sub>3</sub>	.01 - 1.0	2.38	$5 \times 10^{-3}$	2.4
BaF <sub>2</sub>	.15 - .19	1.42	$< 3 \times 10^{-5} - 3 \times 10^{-3}$	1.449
SrF <sub>2</sub>	.7		$4.1 \times 10^{-5} - 1.2 \times 10^{-4}$	1.44

\* ZnSe polycrystalline (CVD)

Note: Value of bulk absorption varies with methods of sample fabrication.

## C. Optical Characterization of Thin Films

### 1. Introduction

As is the case with the window materials, the precise value of the optical absorption coefficient is of critical importance to the survivability and overall performance of high-power anti-reflection or protective coatings. Not only must these films be of high quality from a mechanical and thermal viewpoint, the optical absorption must be as low as possible. It appears, however, that the absorption of thin films always exceeds that of bulk samples of the same material. One possible explanation is that amorphous films are more absorbing in the infrared because of smeared out multiphonon absorption bands. Another, simpler reason would be the presence of impurities or scattering centers in the evaporated film.

Previous investigations of coatings have generally consisted of single-frequency calorimetric loss measurements, which are of little diagnostic use. Optical absorption must be examined over a broad wavelength range to provide information for film diagnostics. Therefore, the internal reflection spectroscopy technique we have used to study optical surface absorption is being used to investigate the infrared absorption of coatings as a function of wavelength. Internal reflection elements are coated for half their width, the infrared transmission of the coated and uncoated halves can then be examined by masking the appropriate portion of the plate. This technique should reveal the presence of impurity bands and other gross changes in the infrared absorption spectrum. Such studies will be aimed at elucidating the difference between the infrared properties of bulk and thin film material.

Infrared absorption can also be determined by using integrated optics coupling techniques, such as prism couplers, to measure transmission as a function of length for a deposited film. Such an approach would relax the limited size and shape requirements associated with the internal reflection method, and permit the nondestructive in situ evaluation of coated windows independent of their physical configuration. In addition, the diagnostic beam of light would be contained largely within the film layer itself rather than

penetrating via an evanescent wave from one side, thus enhancing the interaction. The surface quality and film thickness requirements for high-power laser window applications are comparable with those demanded by integrated optics technology.

## 2. Internal reflection spectroscopy

### a. Introduction

Internal reflection spectroscopy, IRS, is a technique to monitor the optical properties of a material by placing it in contact with a material through which a light beam is propagating while undergoing multiple internal reflections.<sup>1</sup> Figure 5 shows one of many geometries used as reflection elements in IRS. Since the light penetrates a short distance into any material in contact with the internal reflection element and can be absorbed by it, the transmission of the element is determined both by its bulk absorption and by the optical properties of any material in contact with the surface. The theory and the techniques of IRS are described in detail in the excellent book by Harrick.<sup>1</sup> Internal reflection spectroscopy has been used successfully by other investigators<sup>2</sup> to study surface absorption.

### b. Experimental

Internal reflection spectra were obtained using the Harrick ATR plate adaptor attachment in a Perkin Elmer Model 457 infrared spectrometer. Figure 6 shows a schematic diagram of this attachment. For our purpose, the sample holder has been modified so that light passes through only half of the sample. This was done in order to compare the coated and uncoated halves. The ATR plates are 52.5 mm long, 20 mm wide, and 2 mm thick (Fig. 7). One-half the sample (52.5 mm  $\times$  10 mm) is coated with the desired films. Angle  $\theta$  (Fig. 5) was chosen so that light entering the beveled surface will be totally internally reflected. The ATR plates have been received and characterized as described below.

## 3. Substrate characterization

Micrographs of both ZnSe and BaF<sub>2</sub> samples were taken with dark field

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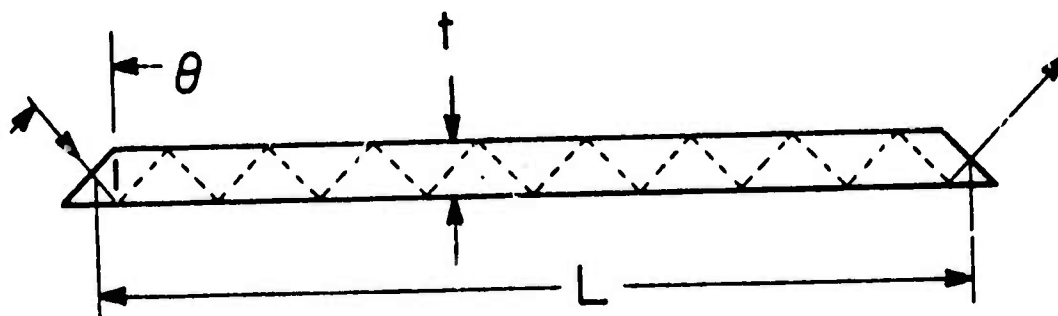
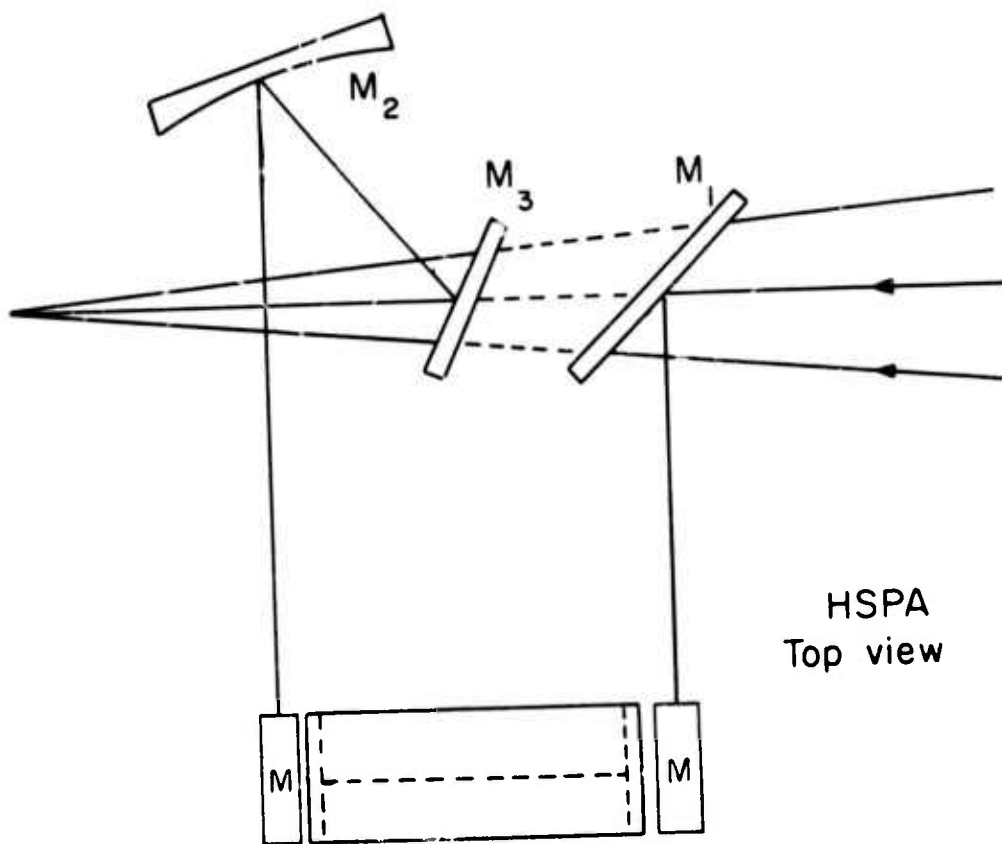
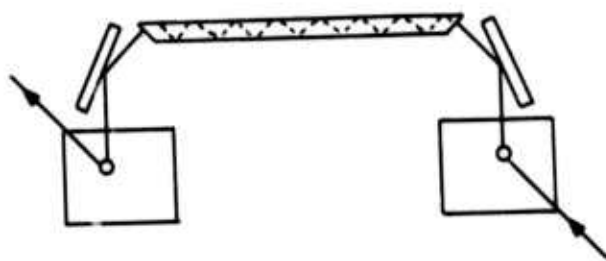


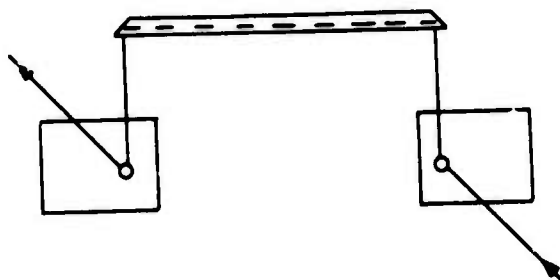
Fig. 5 Internal Reflection Plate.



HSPA  
Top view



IRS mode  
side view



Transmission mode  
side view

Fig. 6 Schematic Diagram of Harrick Scientific  
Horizontal Single Pass Attachment (HSPA).

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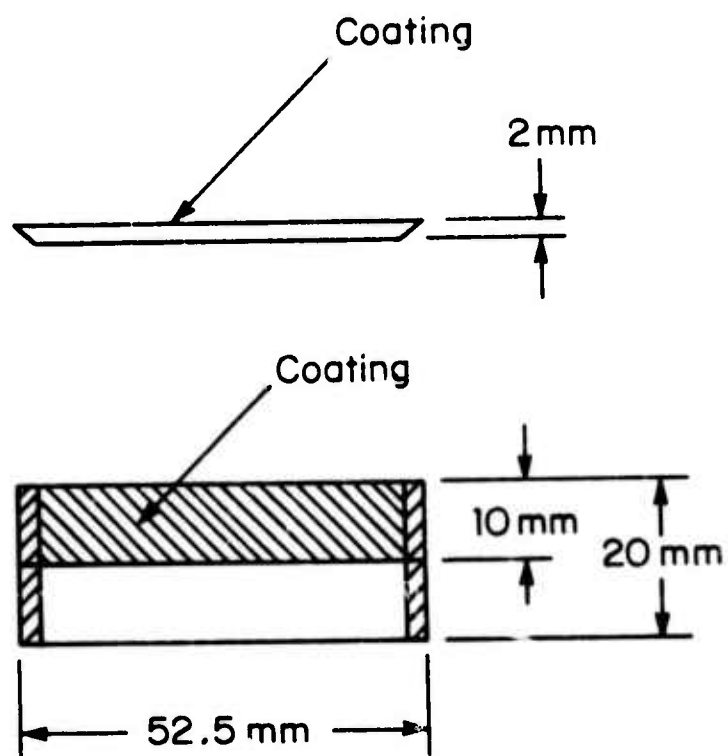


Fig. 7 ATR Plate with Coating.

illumination with a magnification of  $382\times$ . Figures 8 and 9 are typical surfaces of ZnSe and BaF<sub>2</sub> respectively (polished by Harrick). Spectra of the ZnSe and BaF<sub>2</sub> ATR plates were made via internal reflection spectroscopy. Figures 10 and 11 are typical spectral runs.

The broad absorption band centered at  $3350\text{ cm}^{-1}$  is attributed to water,<sup>2</sup> and the sharper structure at  $2915$  and  $2845\text{ cm}^{-1}$ , to C-H stretch vibrations from solvents used in preparing the plates.<sup>3</sup> The absorption at  $1540\text{ cm}^{-1}$  band could correspond to a C = C double bond stretching vibration,<sup>4</sup> while the one at  $1460\text{ cm}^{-1}$  could correspond to a  $\text{C}-\begin{smallmatrix} \text{H} \\ \text{H} \end{smallmatrix}$  bond bending vibration,<sup>5</sup> sometimes referred to as a CH<sub>3</sub> or CH<sub>2</sub> deformation band.

Reductions of these absorption bands can be accomplished with techniques used by T. F. Deutsch and R. I. Rudko.<sup>3</sup> Some of the methods include chemical cleaning, vacuum baking, and plasma cleaning.

Because of lengthy delays in the receipt of our samples, the tests described here have not yet been performed on coated samples.

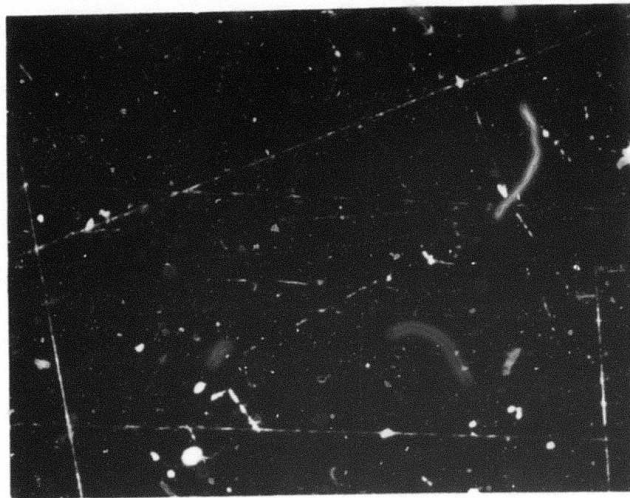
#### 4. IRS spectra of BaF<sub>2</sub> ATR plates coated with As<sub>2</sub>S<sub>3</sub>

Because of the delay in receipt of the BaF<sub>2</sub> and ZnSe ATR plates, we decided to have three existing BaF<sub>2</sub> ATR plates coated with films of As<sub>2</sub>S<sub>3</sub>. Films of  $1/4\lambda$ ,  $1/2\lambda$ , and  $1\lambda$  at  $5\mu\text{m}$  thick were deposited by Broomer Research Lab. Initial work has begun using these samples. Transmission spectra show no absorption other than the expected intrinsic absorption of the BaF<sub>2</sub>.

Internal reflection spectroscopy of these coatings did show a difference between the coated and uncoated surfaces (Fig. 12). Both the uncoated and coated half of the BaF<sub>2</sub> ATR plates show the absorption bands mentioned in Sec. 3, but the coated half of the sample shows a reduction in the intensities of these absorption bands. This is probably due to a cleansing action which occurs during the deposition of the film.



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ZnSe #1

Fig. 8 Typical Surface Finishes of Zinc Selenide ATR Plate.

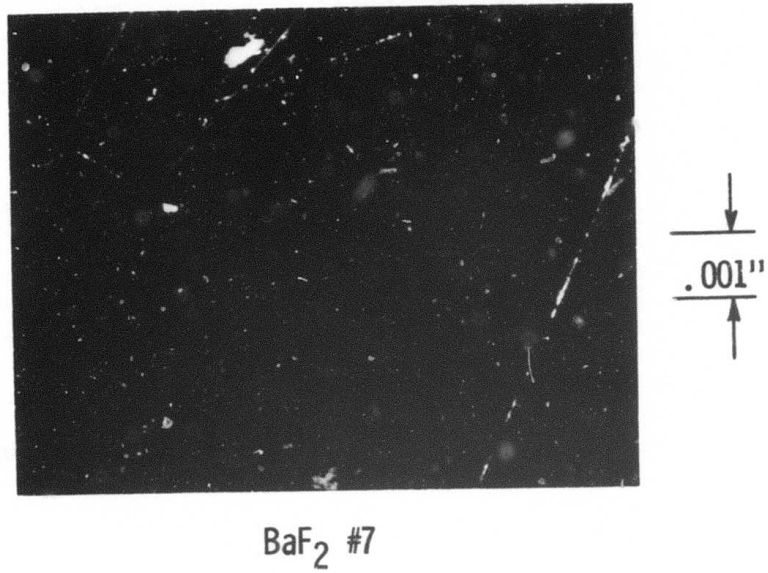


Fig. 9 Typical Surface Finishes of Barium Fluoride ATR Plate.

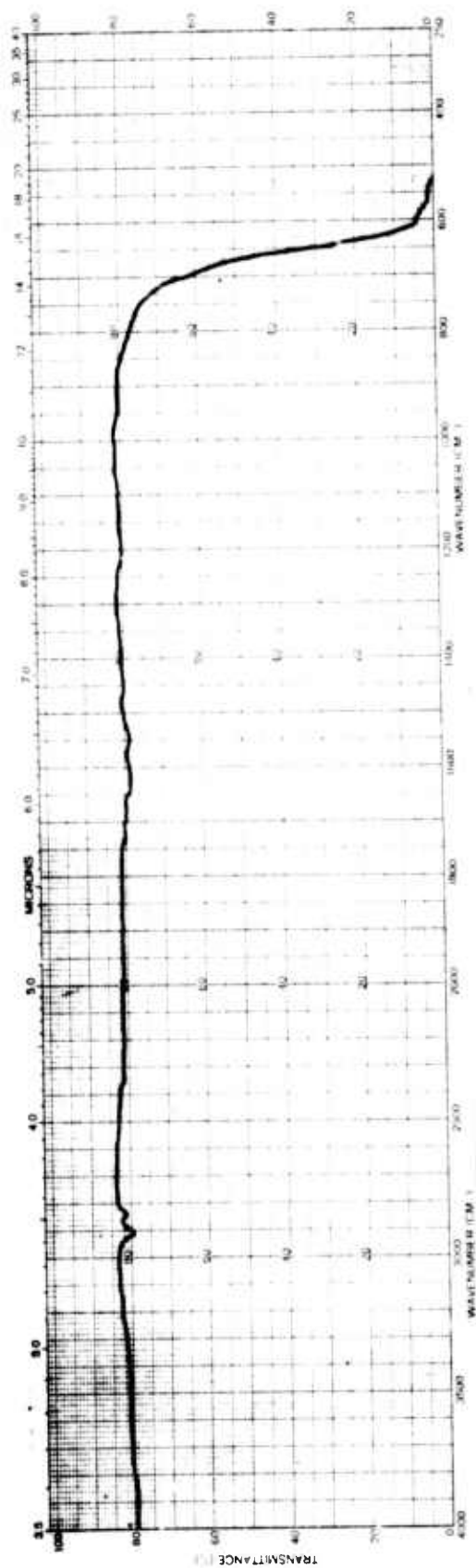


Fig. 10 ZnSe No. 1  $\theta = 45^\circ$  ATR Spectrum.

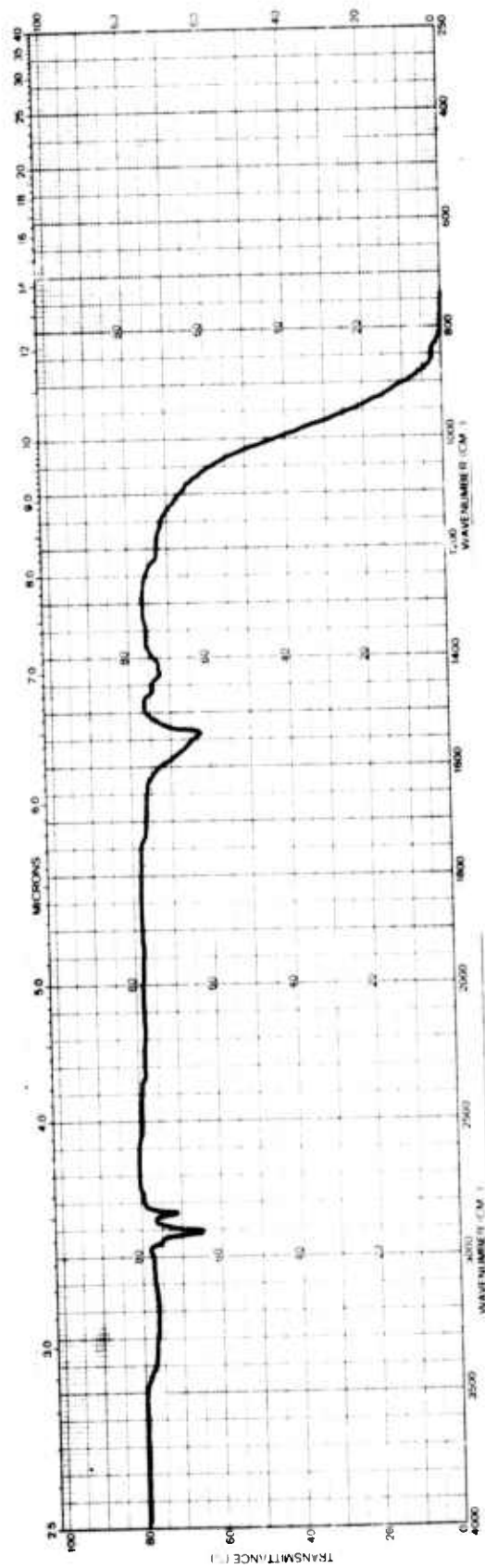


Fig. 11 BaF<sub>2</sub> No. 6 [100]  $\theta = 50^\circ$  ATR Spectrum.

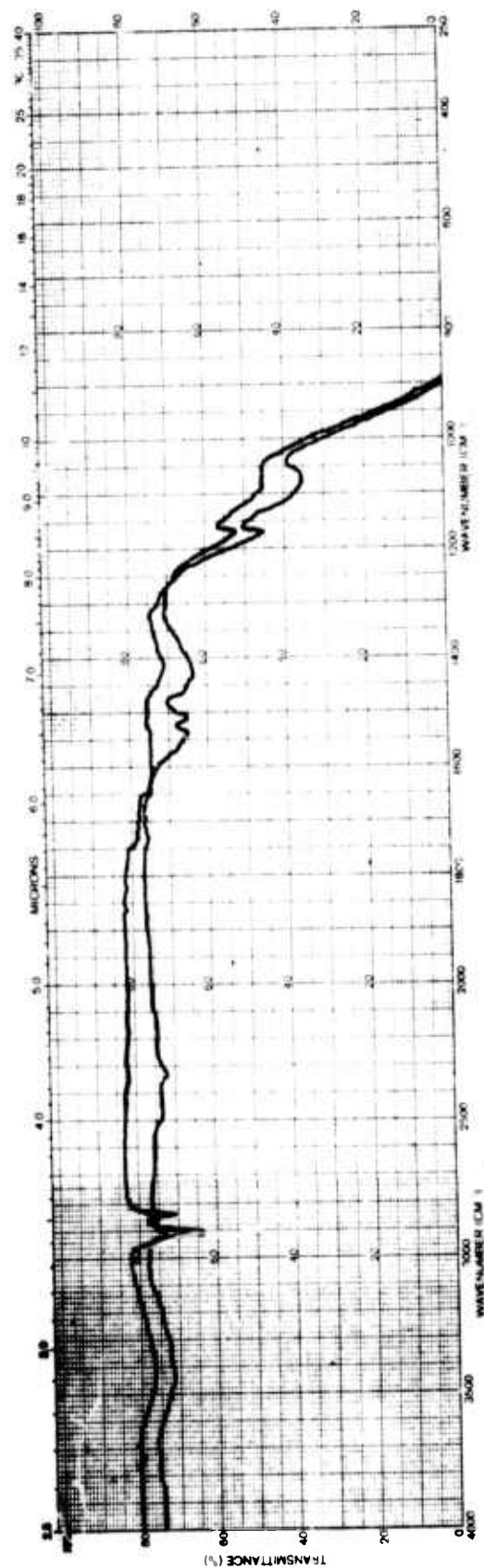


Fig. 12 BaF<sub>2</sub> No. 5  $\theta = 45^\circ$ . Film As<sub>2</sub>S<sub>3</sub> 1/2  $\lambda$  @ 5  $\mu$ m Thick. ATR Spectrum.  
(Upper Curve - without film, Lower curve - with film).

The other differences in the absorption spectra occur near  $1070\text{ cm}^{-1}$ . We believe this is a direct result of the absorption in  $\text{As}_2\text{S}_3$  film, since all the data taken on the three plates exhibit this absorption. There was no other noticeable change in the spectra between  $3\text{ }\mu\text{m}$  and  $5\text{ }\mu\text{m}$ .

Figure 13 shows the bulk transmission spectra of  $\text{As}_2\text{S}_3$  and  $\text{BaF}_2$  samples both 4 mm thick. From these two transmission curves we can construct the combined transmission curve (Fig. 14) for substrate and film. In this construction we shall neglect the effect of Fresnel reflections. The transmission spectra of the  $\text{BaF}_2$  substrate of 4 mm thickness is already given in Fig. 13, and it will be denoted as  $T_1$ . The transmission spectra of the bulk  $\text{As}_2\text{S}_3$  sample has to be corrected for the film thickness. If we denote the bulk thickness as  $L_B$  and the film thickness as  $L_F$ , and if we furthermore denote the transmission of the  $\text{As}_2\text{S}_3$  bulk piece as  $T_2$ , then the combined transmission is

$$T_{\text{combined}} = T_1 \cdot T_2^{L_F/L_B} \quad (1)$$

As expected, this calculation shows that film absorption has little influence on the transmission curve of the substrate material. This type of testing appears to show only gross absorption changes and these would have to be due to contaminants. In the ATR approach the light beam travels many times through the substrate and into the film. The sensitivity of the ATR approach could be enhanced by modifying the ATR plate adaptor by routing the reference beam through the uncoated half of the sample simultaneously as the signal is passed through the coated half. This would cancel out the effect of the substrate material, making the film absorption more predominant. This method will be investigated.

## 5. Integrated optic coupling technique

### a. Introduction

Integrated optic coupling techniques have been used to measure losses in thin films<sup>6,7</sup> at single frequencies. Our approach was to use prism coupling

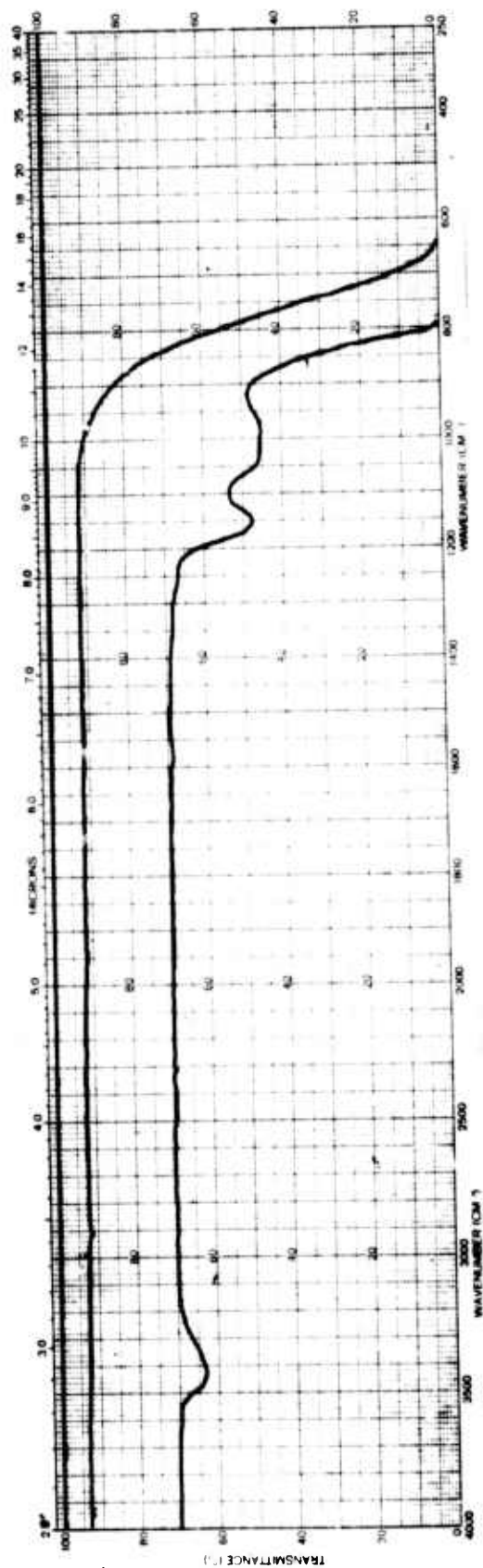


Fig. 13  $\text{As}_2\text{S}_3$  Glass 4 mm Thick,  $\text{BaF}_2$  4 mm Thick Bulk Spectra.  
(Top Curve 100 Percent No sample, Middle Curve  $\text{BaF}_2$   
Spectrum, Bottom Curve  $\text{As}_2\text{S}_3$  Spectrum).

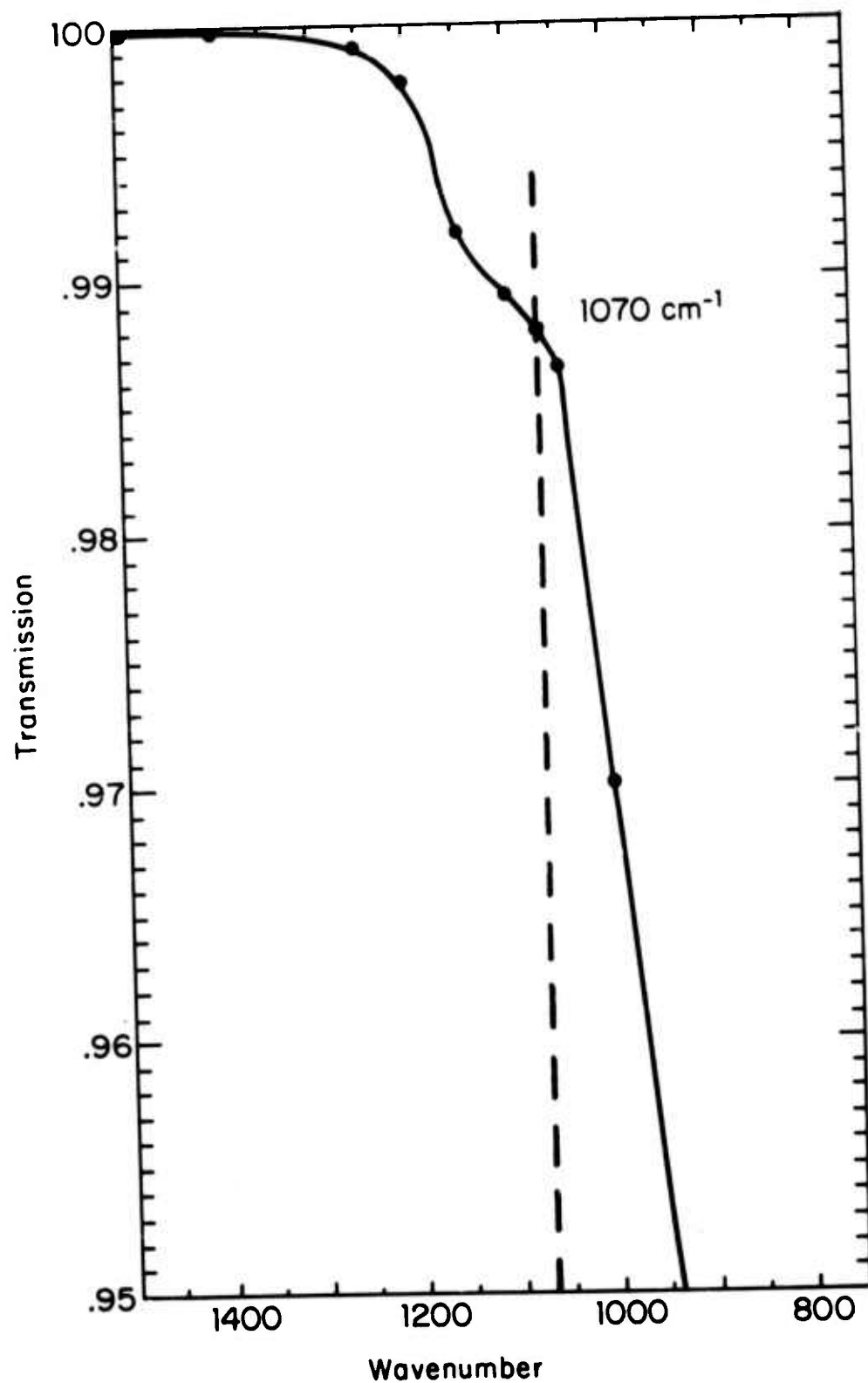


Fig. 14 Combined Transmission Curve for BaF<sub>2</sub> Substrate and As<sub>2</sub>S<sub>3</sub> Film.



of polychromatic light into thin films to measure transmission as a function of wavelength. This approach, if possible, would make absorption spectra of standard coated windows and mirrors feasible. Furthermore, specially fabricated substrates would not be required.

#### b. Experimental

The method described above has been implemented using a HeNe laser (Fig. 15); we have run into a number of problems in our initial tests. The  $\text{BaF}_2$  substrates coated with  $\text{As}_2\text{S}_3$  are of poor quality. Our attempt to propagate light in these films has been unsuccessful due to the immense scattering which occurs due to the poor surface quality of the substrate material. Highly polished substrate material will have to be obtained if coupling is to be attained.

We have looked for a new infrared, broadband point source to be used with this scheme. Past experimenters working in the infrared have used traditional sources such as a globar or a Nernst glower, etc. Since one of the requirements for our source is that it be a point source, these traditional methods were unusable. Because we are trying to couple incoherent light into a thin film for the purpose of measuring the film's spectral absorption, a point source is necessary to focus this light to a compatible spot size for coupling (integrated optic prism coupling). We are experimenting with a miniature, indirectly heated alumina source. A CW  $\text{YAlO}_3$  laser is focused on the end of an alumina rod (Fig. 16). The alumina has been brought up to a temperature of  $2200^\circ\text{C}$ . Spectral analysis of this source shows the radiation from this source exhibits the characteristics of a black body emitter (Fig. 17). The size of the source is controlled by the diameter of the alumina rod and the focusing optics. Tests to see if this source can be coupled into a film have not been made due to the difficulties encountered with standard integrated optic coupling methods using a laser source. Serious consideration will have to be given to this approach if it is to be pursued.

### 6. Calorimetry

#### a. Introduction

Since no obvious absorption in the  $3\mu\text{m}$  to  $5\mu\text{m}$  range could be detected

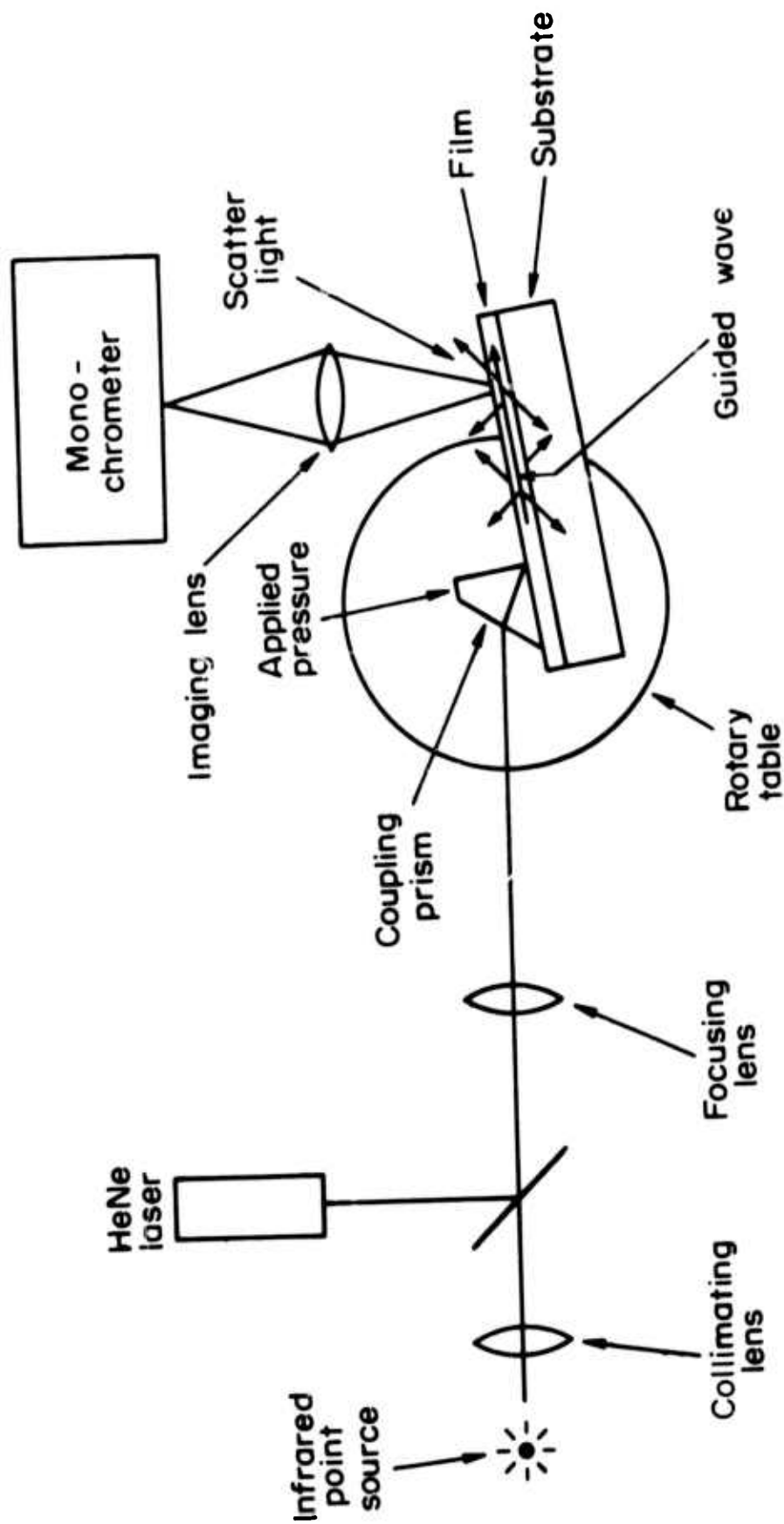


Fig. 15 Basic Integrated Optics Spectral Absorption Technique.

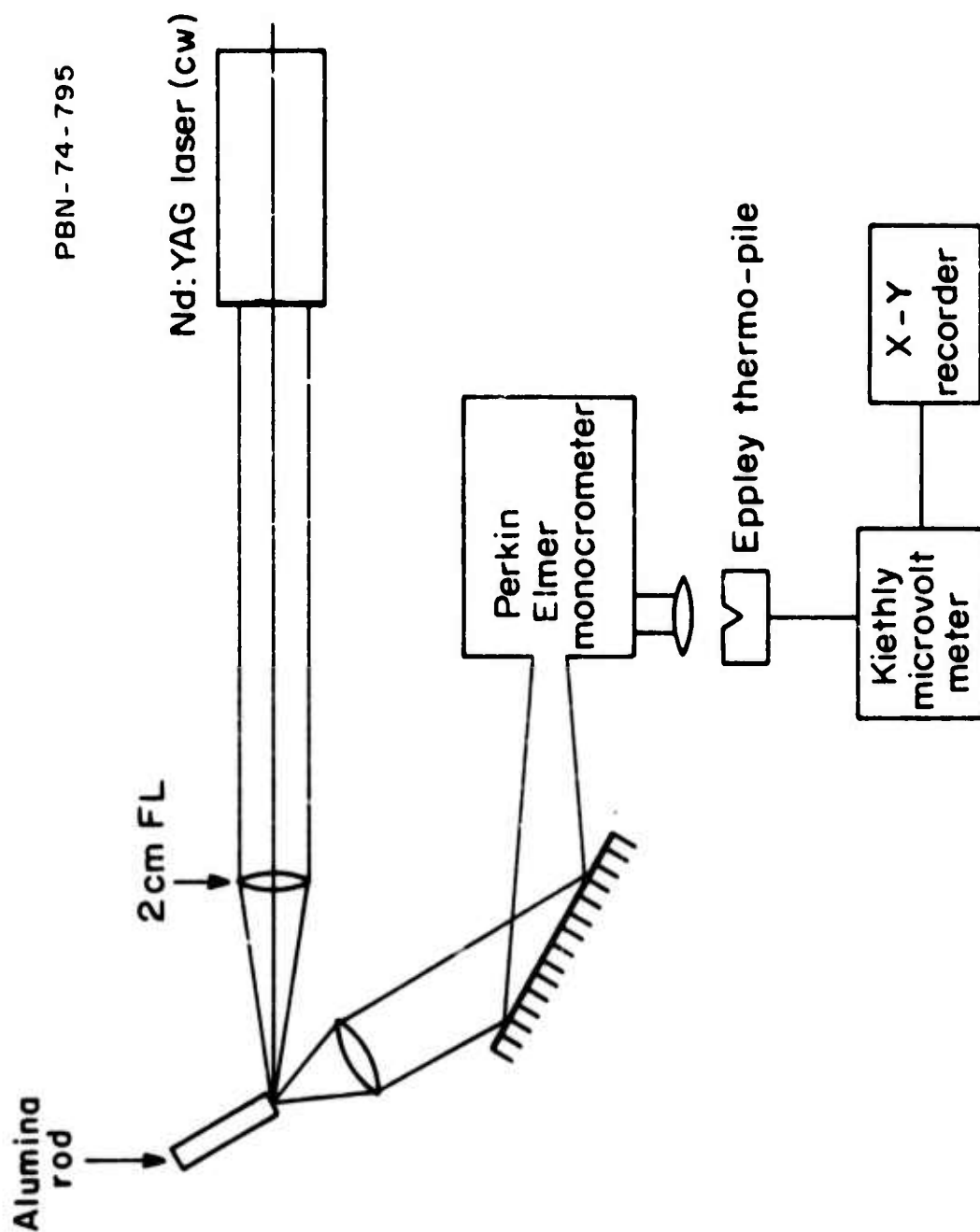


Fig. 16 Infrared Point Source.

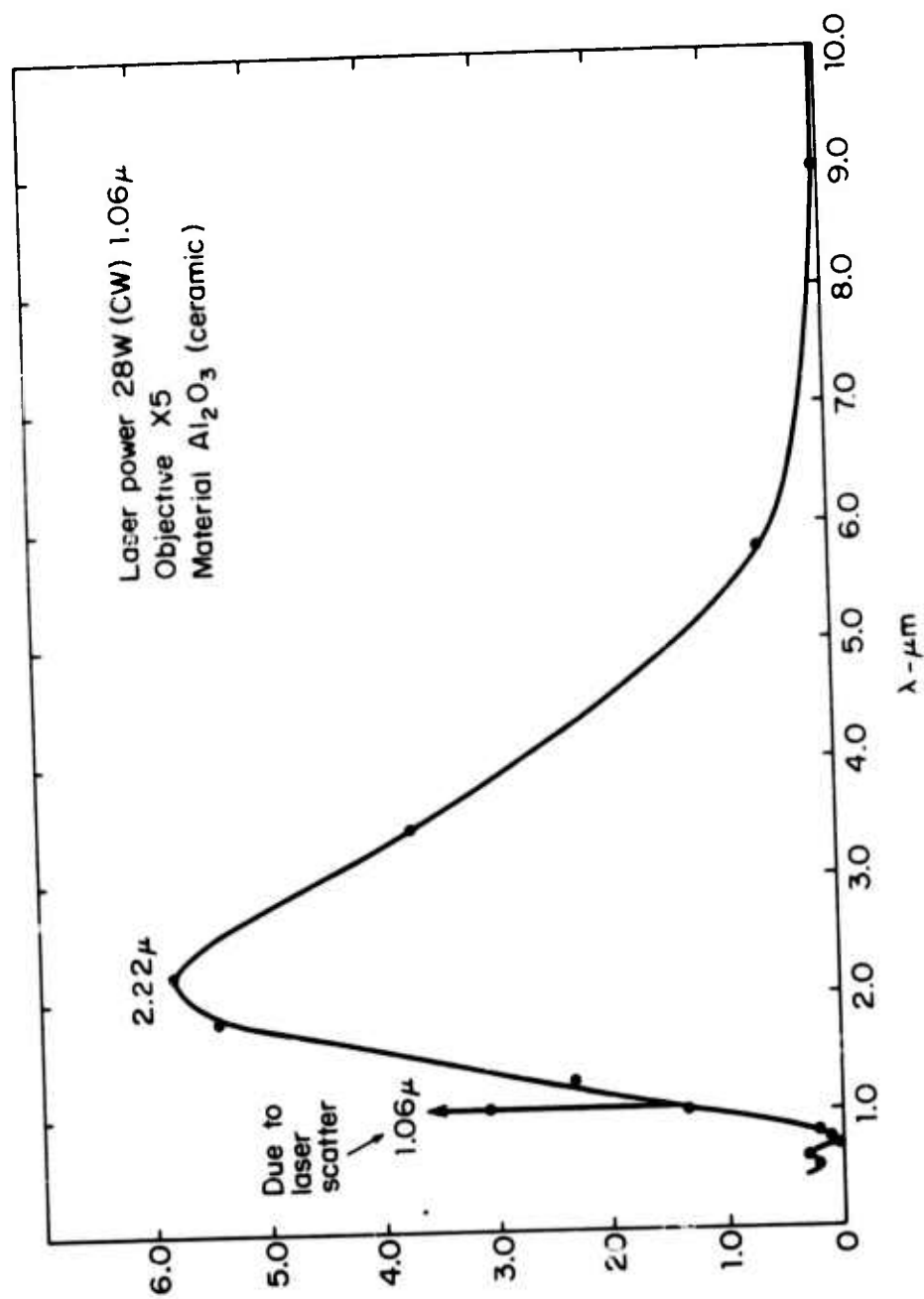


Fig. 17 Output Spectrum of Alumina Point Source.

using internal reflection spectroscopy, calorimetric techniques were used to measure the absorption of the  $\text{As}_2\text{S}_3$  films on the  $\text{BaF}_2$  ATR plates. These techniques can determine the infrared absorption of a low-loss material by measuring the temperature rise of a sample after a given amount of laser energy has passed through it. This method was used to measure the absorption coefficient of the substrate and the substrate/film combination.

## b. Theory

Most measurements of film absorption are made by measuring the substrate material and then the film/ substrate combination; the difference is given as a percentage increase in the absorption. However, this interpretation is oversimplified since the film changes the surface reflection and thus the power incident on the substrate. What is really needed is the absolute value of the absorption coefficient of the film. To obtain this, the  $\beta$  (absorption coefficient) of the substrate must first be known.

The power absorbed by a substrate of thickness  $\ell$ , and absorption coefficient  $\beta$  when  $\beta \ell$  is small is

$$P_{\text{absorbed}} = P_{\text{inside}} (1 - e^{-\beta \ell}) \quad . \quad (2)$$

For  $\beta \ell \ll 1$ , this equation becomes

$$P_{\text{absorbed}} = \beta \ell P_{\text{inside}} \quad . \quad (3)$$

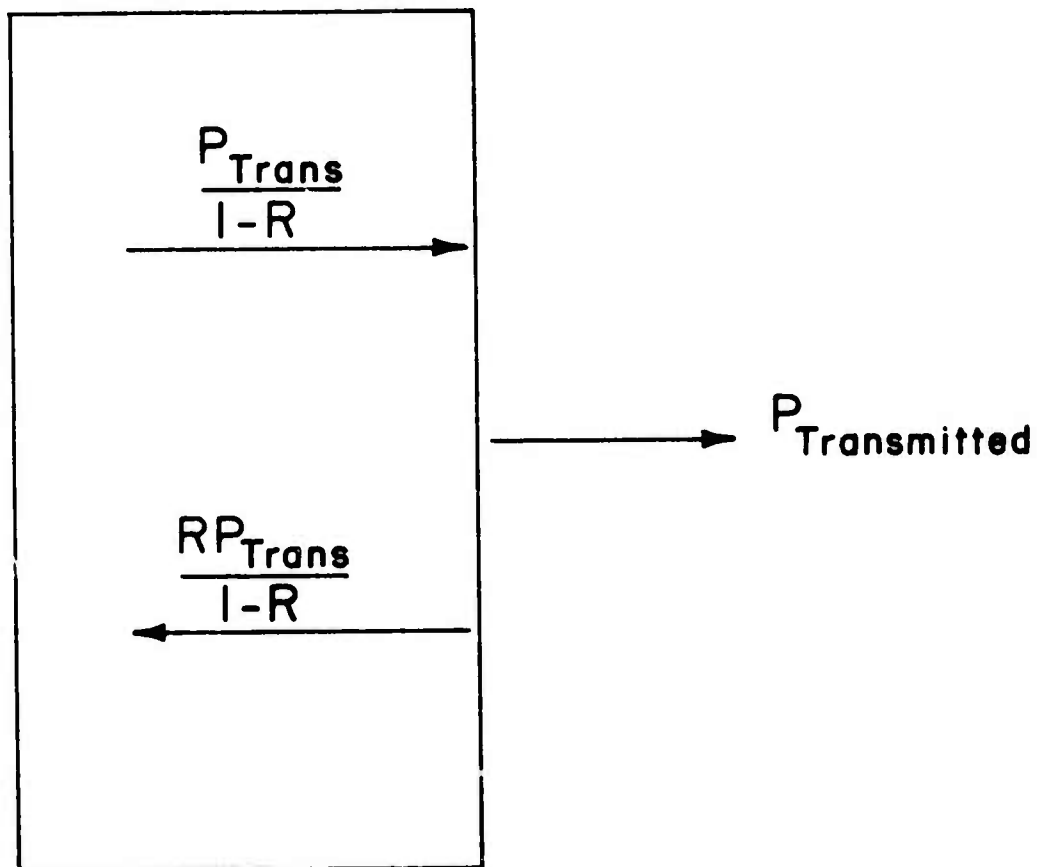
Figure 18 shows the calculation of  $P_{\text{inside}}$  (the power inside the sample). If the transmitted power and the index of refraction of the sample are known, we can determine the two components of power, i. e., a wave traveling toward the exit surface and a reflected wave, whose sum is the total power in the sample.

Substituting the result from Fig. 18 into Eq (3) gives

$$P_{\text{absorbed}} = \beta \ell P_{\text{tran}} \left( \frac{1+R}{1-R} \right) = \beta \ell P_{\text{tran}} \frac{n^2+1}{2n} \quad , \quad (4)$$

or

$$\beta = \frac{1}{\ell} \frac{P_{\text{absorbed}}}{P_{\text{transmitted}}} \left( \frac{2n}{1+n^2} \right) \quad . \quad (5)$$



$$P_{Inside} = P_{Trans} \times \frac{(1+R)}{(1-R)} \quad R = \left(\frac{n-1}{n+1}\right)^2$$

$$P_{Inside} = P_{Trans} \times \left(\frac{n^2+1}{2n}\right)$$

Fig. 18 Calculation of Power Inside Sample.

Again, this equation for the absorption coefficient,  $\beta$ , assumes  $\beta \ell \ll 1$ . To determine the usefulness of this assumption, the exact equation for the absorption coefficient was calculated

$$\beta = \frac{1}{\ell} \ln \left\{ \frac{(2n) ((P_{\text{abs}}/P_{\text{tran}}) + 1)}{(n+1)^2} \left[ 1 + \sqrt{1 + \left[ \frac{n^2 - 1}{2n (P_{\text{abs}}/P_{\text{tran}} + 1)} \right]^2} \right] \right\} \quad (6)$$

This equation is plotted in Fig. 19 together with the approximate Eq. (5); for an index of refraction of 1.40 the two equations deviate about five percent for  $\beta \ell = 0.1$ . Thus for  $\beta \ell < 0.1$ , the approximate equation can be used and for  $\beta \ell$  greater than 0.1 the exact equation should be used. Both of these equations are independent of the coherence of the infrared beam and the possibility of interference fringes because the absorption coefficient is determined from the transmitted power and the reflectivity of the rear surface of the sample. The incident power can only be used to calculate the power inside the sample if the IR beam is incoherent. If it is coherent, resonance effects can change the ratio of  $P_{\text{inside}}$  to  $P_{\text{incident}}$  making it difficult to do the calculation. Therefore, our experimental apparatus is set up to measure transmitted power.

Once the  $\beta_s$  for the substrate is known, one can calculate the  $(\beta_F)$  absorption coefficient of the film.

In the following, we want to derive the formulas necessary to evaluate the absorption of the surface film from calorimetric measurements. As shown in conjunction with Fig. 18, the absorbed laser power in a simple uncoated slab of material is given in terms of the absorption coefficient  $\beta_s$  of the substrate, the thickness of the substrate  $L_s$ , the reflection coefficient of the surface  $R_s$  by

$$P_{\text{abs}} = \beta_s L_s \frac{1+R_s}{1-R_s} P_{\text{trans}} \quad (7)$$

We can conveniently generalize this equation to cover the absorption both in the substrate and in the film if we orient the sample such that the film is at the exit side of the laser beam. The total film acts like a Fabry-Perot reflector of as yet unknown reflectivity  $R_F$ . Thus, Eq. (8) gives the absorption in the substrate if we replace  $R_s$  by the film reflectivity  $R_F$

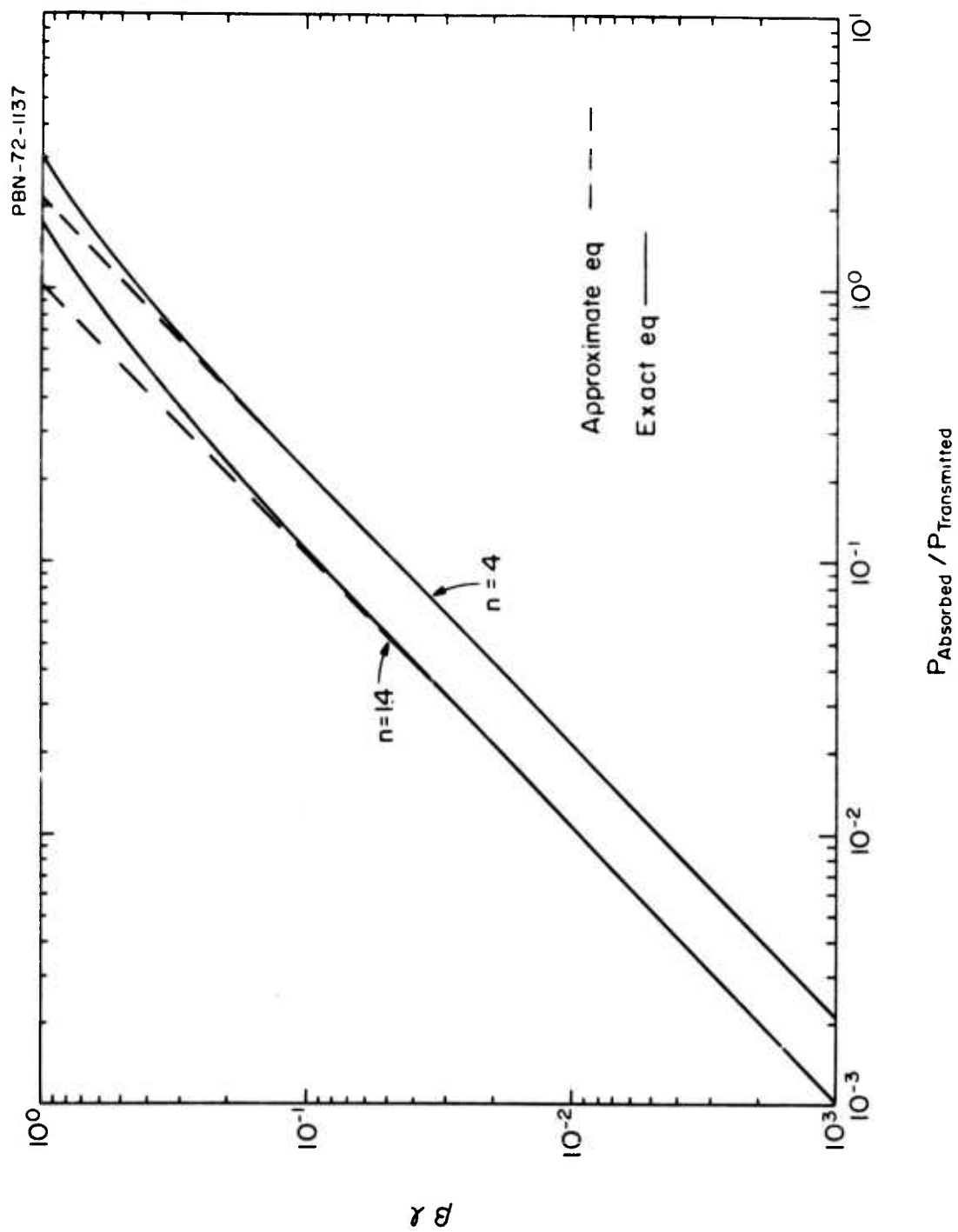


Fig. 19 Exact Equation and Approximate Equation for Absorption Coefficient.



$$P_{\text{abs}}(\text{substrate}) = \beta_s L_s \frac{1+R_F}{1-R_F} P_{\text{trans}} \quad (8)$$

We can also use Eq. (7) to calculate the power absorbed in the film by interpreting  $R_s$  as the reflectivity at the air-film interface  $R_{FA}$ . We must also change  $\beta_s$  to the absorption coefficient of the film  $\beta_F$  and the length  $L_s$  to the film thickness  $\Delta L_F$ . Thus,

$$P_{\text{abs}}(\text{Film}) = \beta_F \Delta L_F \frac{1+R_{FA}}{1-R_{FA}} P_{\text{trans}} \quad (9)$$

The total absorption in substrate and film follows by adding Eqs. (8) and (9)

$$\frac{P_{\text{abs}}}{P_{\text{trans}}} = \beta_s L_s \frac{1+R_F}{1-R_F} + \beta_F \Delta L_F \frac{1+R_{FA}}{1-R_{FA}} \quad (10)$$

By noting that

$$R_{FA} = \left( \frac{n_F - 1}{n_F + 1} \right)^2 \quad (11)$$

where  $n_F$  is index of refraction of the film, we obtain

$$\frac{P_{\text{abs}}}{P_{\text{trans}}} = \beta_s L_s \frac{1+R_F}{1-R_F} + \beta_F \Delta L_s \frac{n_F^2 + 1}{2n_F} \quad (12)$$

We now define an effective  $\bar{\beta}_s$  including substrate and film by the equation

$$\frac{P_{\text{abs}}}{P_{\text{trans}}} = \bar{\beta}_s L_s \frac{n_F^2 + 1}{2n_F} \quad (13)$$

Equating Eqs. (12) and (13) gives

$$\beta_F = \frac{L_s}{\Delta L_F} \left[ \bar{\beta}_s - \beta_s \left( \frac{2n_F}{n_F^2 + 1} \right) \frac{1+R_F}{1-R_F} \right] \quad (14)$$

Equation (14) is the basis for determining  $\beta_F$  from measurements. In essence  $\beta_s$  is determined by measuring the absorbed power in the uncoated substrate and using Eq. (7) with

$$R_s = \left( \frac{n_s - 1}{n_s + 1} \right)^2 \quad (15)$$

Furthermore,  $\beta_s$  is determined from Eq. (13) with measurements carried out on the coated sample. The quantity  $R_F$  is being measured by monitoring the transmission of light through the sample. The necessary equations for this measurement are derived in the following. In Fig. 20 we show light of intensity  $P_o$  falling on the uncoated side of the substrate. The light transmitted into the substrate is  $(1-R_s) P_o$ . Upon the first reflection from the film, the amount of light transmitted is given by  $(1-R_s)(1-R_F) P_o$ . We can add up all transmitted light waves after bouncing back and forth in the substrate neglecting the phase factors (because of the large thickness) to give

$$\begin{aligned} \frac{P_{\text{trans}}}{P_o} &= (1-R_s)(1-R_F) (1 + R_F R_s + R_F^2 R_s^2 + \dots) \\ &= \frac{(1-R_s)(1-R_F)}{1-R_s R_F} \end{aligned} \quad (16)$$

By defining a transmissivity  $T$  through

$$\frac{P_{\text{trans}}}{P_o} = T \quad (17)$$

we obtain from Eqs. (15) and (16)

$$R_F = \frac{1-R_s-T}{1-R_s-TR_s} \quad (18)$$

Experimentally we measure  $T$  and using  $R_s$  from Eq. (15) we obtain  $R_F$ . Thus, all factors are in hand to determine  $\beta_F$  in Eq. (14).

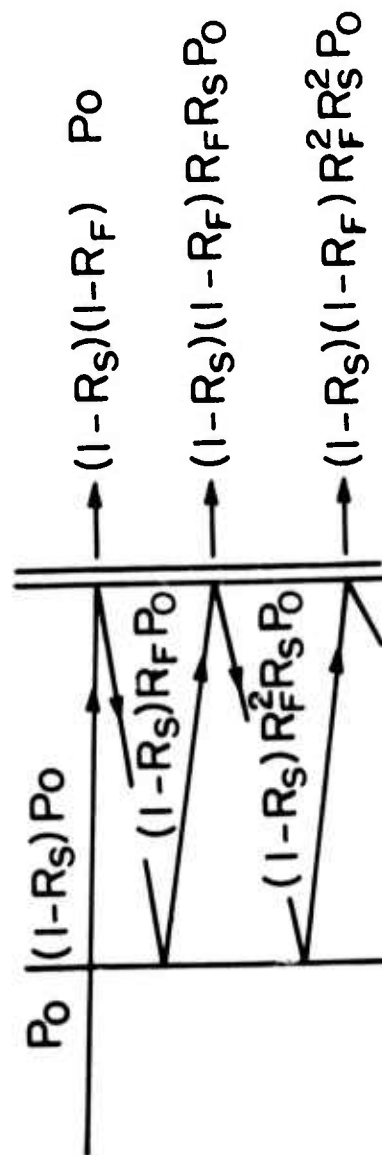


Fig. 20 Calculation of Film Reflection from Transmitted and Incident Laser Power.

### c. Experimental apparatus

Figure 21 shows a schematic view of the entire system, while Fig. 22 shows a diagram of the calorimeter chamber. The calorimeter chamber is rectangular with a one-inch thick plexiglas cover. The outside dimensions of the chamber, which is made of 1/2 in. thick aluminum, are approximately  $13 \times 14 \times 25$  in. An optical rail is mounted within the chamber and the various components, such as irises, sample mounts, and the power cone are mounted on optical carriers with adjustable x-y motions, permitting ready removal of alignment of any component. The chamber vacuum is evacuated by three 50 cfm pumps.

As shown in Fig. 21, a He-Ne alignment laser has been permanently incorporated into the system; a flip mirror allows the beam to be directed along the same axis as the measurement lasers. Preliminary sample alignment is performed using the visible laser, and the final alignment is checked using burn spots made by the infrared lasers.

A sealed  $\text{CO}_2$  laser, designed for single-mode operation and producing about 20W, was installed. The sealed CO laser uses a dry-ice and methanol cooling system and is capable of producing 20W of multimode power.

Either the CO or the  $\text{CO}_2$  laser beam can be directed into the chamber by using a flip mirror; this allows the same sample to be measured at both wavelengths without removing it from the chamber. As the CO laser can operate on a number of transitions in the  $5\mu\text{m}$  region, a 0.5m grating monochromator was incorporated into the measurement system to allow frequent wavelength checks. A Au:Ge detector cooled with liquid nitrogen, a tuning fork chopper, and a lock-in amplifier comprise the detection system.

As we did not know how much the spectral output of the CO laser would vary with time, a number of measurements of the output spectrum were taken. Figure 23 shows the spectra obtained when the output was examined on several successive days. The center of gravity of the output spectrum is relatively constant and is estimated to be  $5.25\mu\text{m}$ . This number is used below as the nominal wavelength of the CO laser.

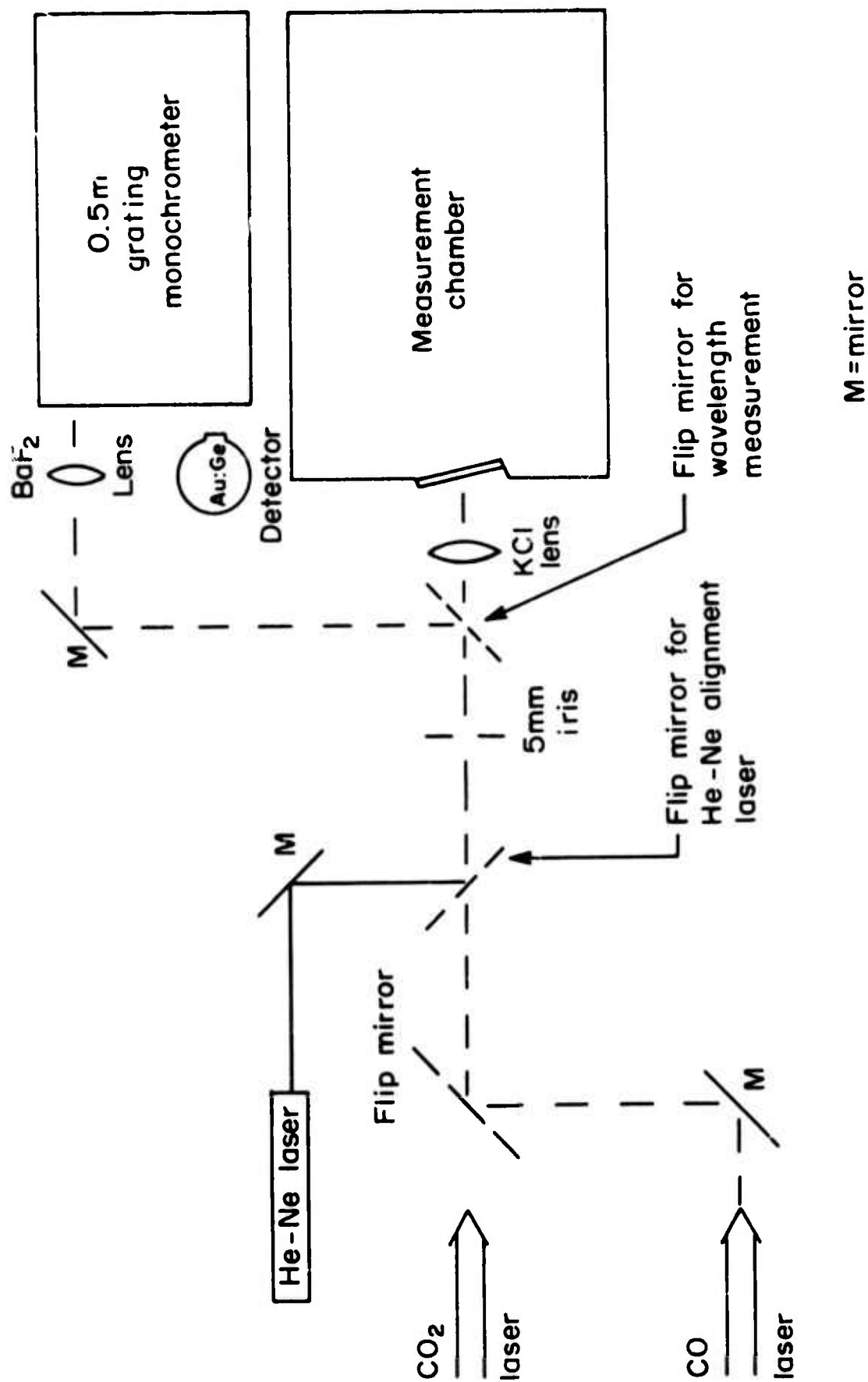


Fig. 21 Schematic Diagram of the Calorimetric Measurement System.

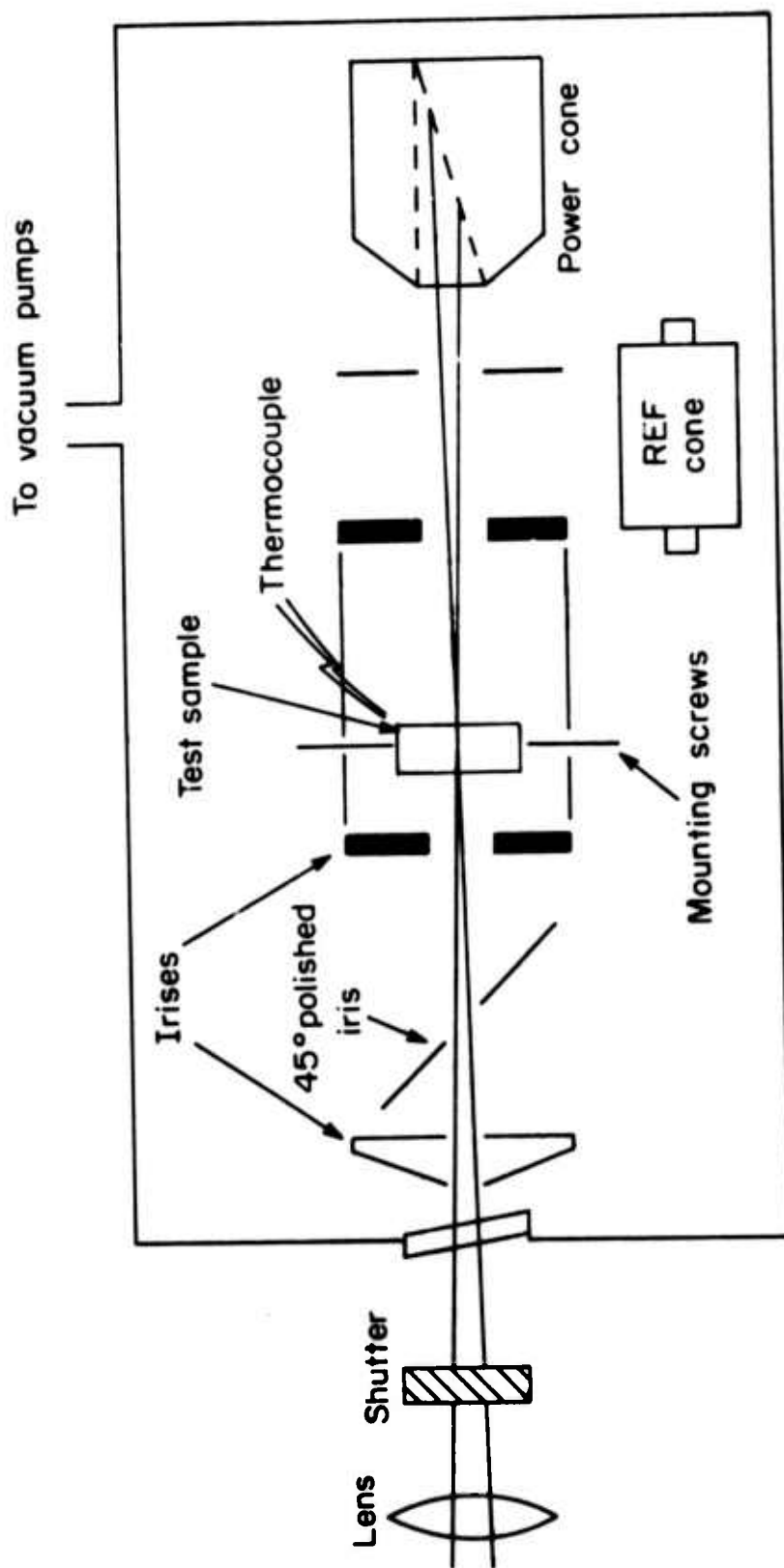


Fig. 22 Schematic Diagram of CO<sub>2</sub>/CO Laser Calorimeter Chamber.

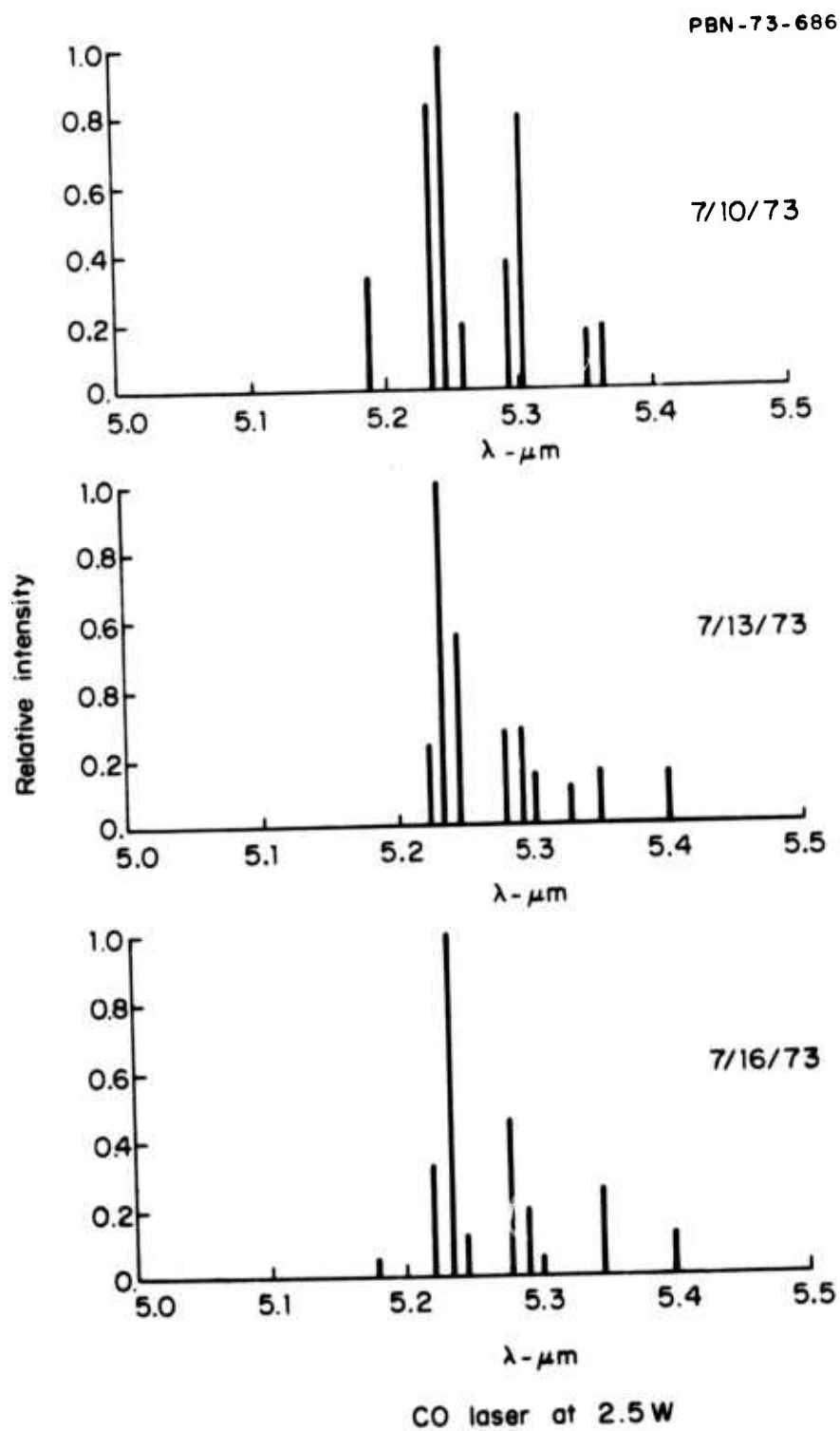


Fig. 23 Spectral Output of the CO Laser on Three Successive Days.

An 18-inch focal-length KCl lens is used to focus the beam into the sample. Reflections from the faces of the sample are directed onto a polished iris which is angled at  $45^\circ$  to the main beam and reflected onto the blackened chamber walls. The sample itself is mounted by three or four nylon screws within a 3-inch-diameter piece of aluminum tubing, the ends of which are closed off by irises. This prevents stray radiation which is not on the beam axis from reaching the sample thermocouple; the latter is further covered by a small piece of aluminum foil to reduce any direct absorption of stray radiation.

The power cone was designed to avoid possible reflections from the tip and to reduce the power density on the cone. Figure 24 shows the design, which reduces the power density by using a sharply cut ( $15^\circ$ ) wedge pressed into a separate outer piece; any reflections that do occur will not return along the incident beam. The thermocouple is clamped inside the aluminum block as shown, assuring good thermal contact and minimizing the turn on/ turn off transients which can make the power cone temperature versus time curves hard to interpret. The cone was checked against the readings given by a CRL power meter at the same location within the chamber and the two techniques were found to agree to better than 5 percent.

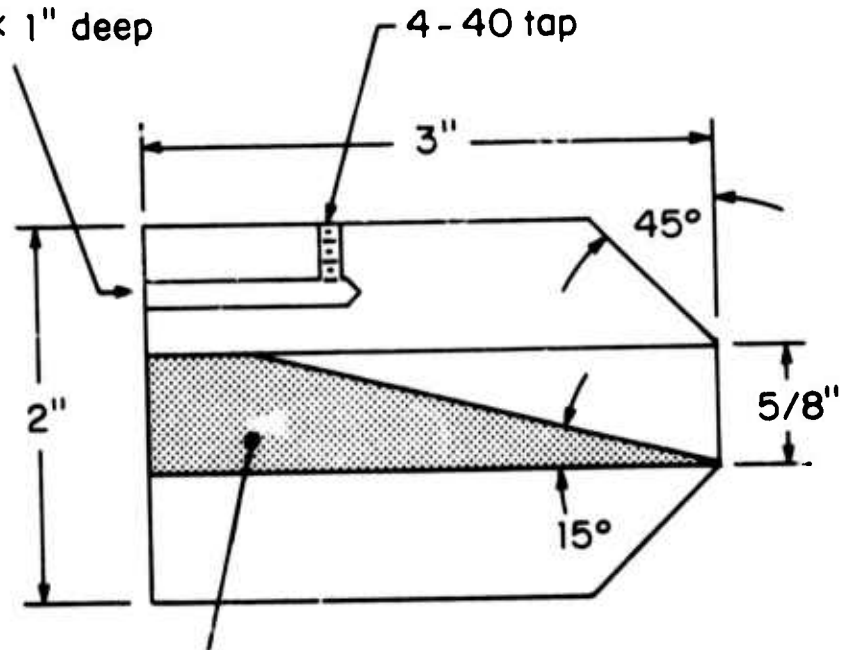
A Keithley Model 148 nanovoltmeter is used to measure the output of the copper-constantan sample thermocouples. The noise and drift of this instrument was less than  $10^{-8}$  volts during the run, well below the  $10^{-7}$  volt sample signals encountered with very low loss samples.

#### d. Results

$\text{BaF}_2$  ATR plate No. 4 coated on one side with  $1/4\lambda$  at  $5\mu\text{m}$  of  $\text{As}_2\text{S}_3$  was measured at  $5.25\mu\text{m}$ . The calorimetric measurements of the uncoated side of the  $\text{BaF}_2$  ATR plate are necessary because the absorption coefficient  $\beta_s$  of the substrate is needed in order to calculate the absorption coefficient of the film ( $\beta_F$ ). Figure 25 shows the sample temperature rise in microvolts at  $5.25\mu\text{m}$ . The data taken from the curves have been corrected for both the initial transient response of the sample and possible error due to drifting. From these curves we can determine the temperature rise  $\Delta T$  and hence absorption coefficient using the calculations in Sec. 4.



Hole for thermocouple  
1/8" dia × 1" deep



Shaded piece is 5/8" nominal dia , cut at 15°, sand blasted , and pressed into outer piece - outer surface polished

Fig. 24 Diagram of Aluminum Power Cone.

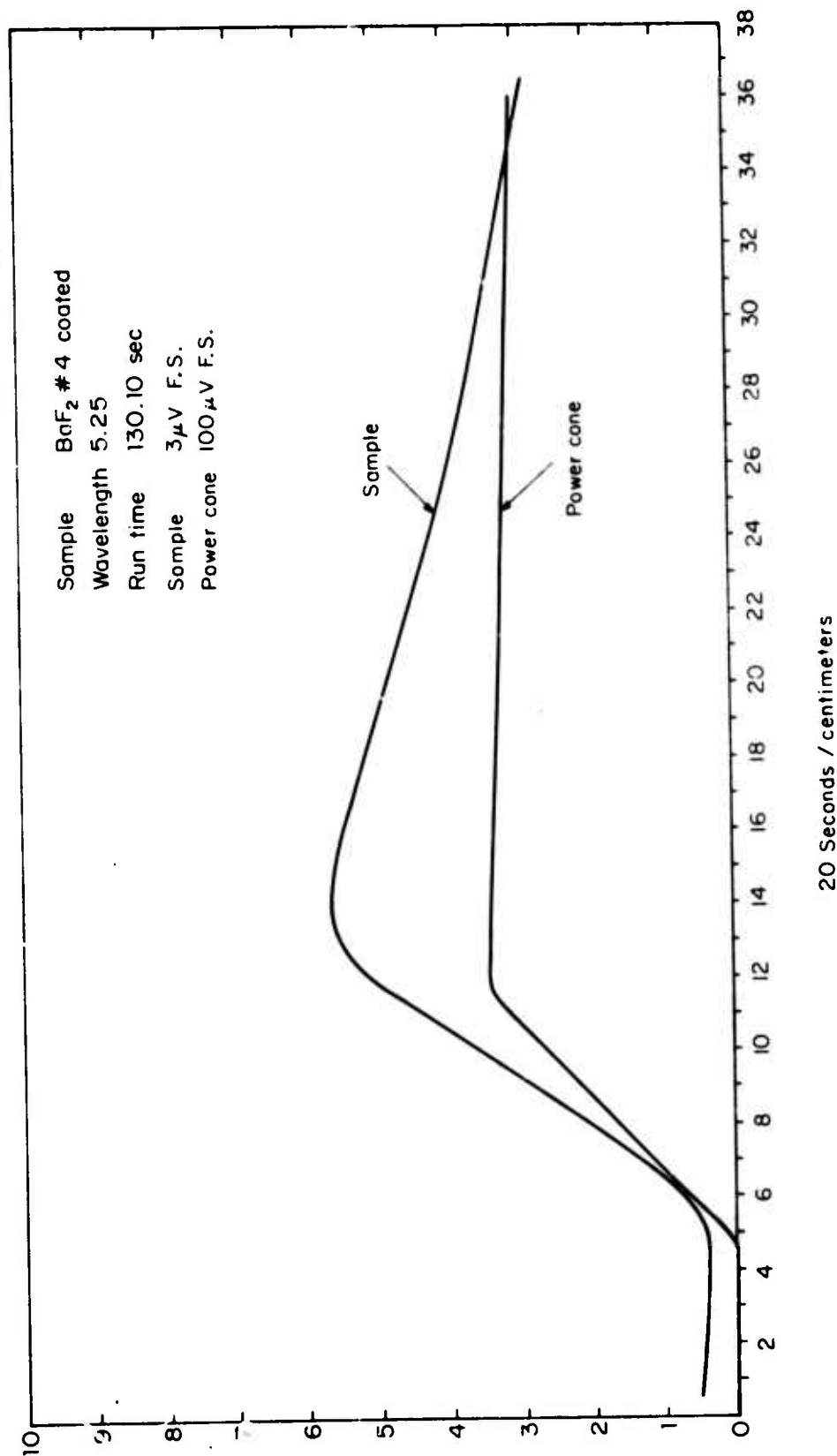


Fig. 25 Typical Temperature Rise of Sample and Power Cone in Microvolts.

The experimental absorption coefficient  $\beta_s$  for BaF<sub>2</sub> No. 4 uncoated was  $7.35 \times 10^{-4} \text{ cm}^{-1}$ . The same experiment was made on the coated side of the sample. The results of this experiment produced combined absorption coefficient  $\bar{\beta}_s$  of  $1.47 \times 10^{-3} \text{ cm}^{-1}$ . With the results of these two experiments and transmission data made on the film/ substrate, one can calculate an absorption coefficient ( $\beta_F$ ) of the film (using Eq. (14)) of  $1.617 \text{ cm}^{-1}$ .

$$\beta_F = \frac{L_s}{\Delta L} \left[ \bar{\beta}_s - \beta_s \left( \frac{2n_F}{n_F^2 + 1} \right) \left( \frac{1 + R_F}{1 - R_F} \right) \right] \quad (19)$$

$L_s$  = substrate thickness

$\Delta L$  = film thickness

$n_F$  = index of the film

The results of calorimetric measurements at both  $10.6 \mu\text{m}$  and  $5.25 \mu\text{m}$  are summarized in Table II. Obviously at  $10.6 \mu\text{m}$  we cannot measure the absorption with any reliability with the present specimens. The problem is this: The bulk substrate absorbs approximately one thousand times as much laser energy as the film. We therefore have to determine the absorbed power with an accuracy of 0.01 percent in order to get meaningful answers. This accuracy is not achieved in our present calorimetric setup. If we want to get an answer we would have to thin down the BaF<sub>2</sub> substrate by at least a factor of ten. In any case, the strongly absorbing substrate of BaF<sub>2</sub> is not suitable for high power windows at  $10.6 \mu\text{m}$ .

Measurements on a ZnSe substrate show a very low loss at  $10.6 \mu\text{m}$  ( $> 10^{-3} \text{ cm}^{-1}$ ) and no such difficulties are expected.

#### D. Mechanical and Physiochemical Properties of Thin Films

##### 1. Introduction

At present, the mechanical properties of optical coatings are evaluated by relatively crude methods such as scotch tape and eraser rub tests for film adherence. While these tests are economical and simple, they are not well defined techniques capable of ready comparison between laboratories. We are investigating the ways of characterizing mechanical and physical properties of optical films with the goal of finding some more quantitative characterization

TABLE II

RESULTS OF CALORIMETRIC EXPERIMENTS FOR FILM OF  
As<sub>2</sub>S<sub>3</sub>(ARSENIC TRISULFIDE)

<u>Sample</u>	<u>Film Thickness</u>	<u>10.6μm (CO<sub>2</sub> Laser)</u>		
		<u>β<sub>s</sub> (cm<sup>-1</sup>)</u>	<u>β<sub>s</sub> (cm<sup>-1</sup>)</u>	<u>β<sub>F</sub> (cm<sup>-1</sup>)</u>
BaF <sub>2</sub> No. 4	.62μ	.151	.170	Neg. Number
BaF <sub>2</sub> No. 5	1.18μ	.128	.159	Neg. Number
<u>5.25μm (CO Laser)</u>				
BaF <sub>2</sub> No. 4	.62μ	7.35 × 10 <sup>-4</sup>	1.47 × 10 <sup>-3</sup>	1.619
BaF <sub>2</sub> No. 5	1.18μ	7.55 × 10 <sup>-4</sup>	2.065 × 10 <sup>-3</sup>	2.59

tests. Some of the properties of interest are film adhesion, hardness, resistance to attack by cleaning liquids and freedom from pinholes and inclusions. Some possible characterization techniques include the use of a diamond scribe, with known loading, to test scratch resistance in conjunction with a scanning electron beam microscope and the use of an epoxy adhesive bond with a known load to measure film adhesion.

## 2. Film adhesion

The adhesion of coatings on substrate materials is an important physical parameter. A part of this program is to find a technique or improve on a known technique for measuring the adhesions of thin films to their substrates. After surveying the literature, we decided to test two methods - the direct pull method<sup>8</sup> and the pull tab method.<sup>9</sup>

### a. Direct pull method

The first is a direct pull method, by which a glass rod is epoxied to a thin film and a measurable force is applied to the rod until the film pulls from the substrate (Fig. 26). After experimenting with the adhesive strength of different epoxies, we decided to use Able Bond 660-6, a liquid which is heat-cured at 120°C.

The direct pull method has been tested on  $\text{SiO}_2$  films deposited on BK-7 glass, Ti/Au films deposited on BK-7 glass and  $\text{As}_2\text{S}_3$  film deposited on  $\text{BaF}_2$ . Both films of  $\text{SiO}_2$  and Ti/Au on BK-7 glass had adhesion strengths greater than 7000 lb/in<sup>2</sup> exceeding the tensile strength of the epoxy (Able Bond 660-3). In one experiment a piece of the fused quartz pull-rod was removed. We were able to pull the  $\text{As}_2\text{S}_3$  film (1λ at 5 μm) from the  $\text{BaF}_2$  substrate with a force of 397 lb/in<sup>2</sup>.

The problem we face with this type of testing is basically the same which other experimenters have run into, reproducibility.<sup>8,9</sup> We are presently trying to refine this technique.

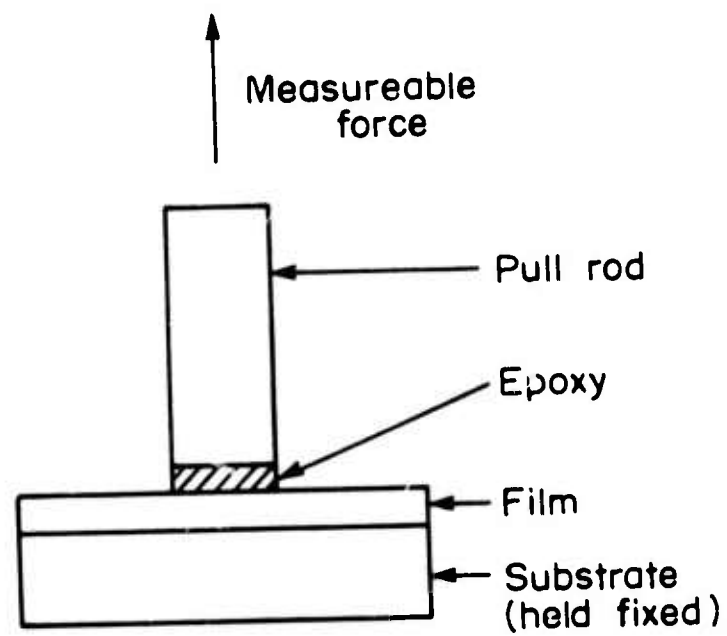


Fig. 26 Film Adhesion Experiment, Direct Pull Method.

### b. Pull tab method

Another method under investigation is the pull tab approach (Fig. 27) by which a  $1/2$  in.  $\times$   $1/4$  in. Cr/Au tab is deposited on a dielectric film. The deposition is done so that only a quarter-inch square actually adheres to the film leaving the other quarter-inch square accessible for pulling. As yet this approach has not been successful. A new method will have to be devised so that the tabs are made more durable for pulling. If successful, this approach would be limited to poorly adhering films. However, the pull tab method most readily gives the single quantity that defines adhesion, i.e., the surface or interface energy.

An excellent article on the physical mechanisms underlying the various pull-off, pull and scratch adhesion tests has been published by K. Kendall.<sup>10</sup>

### 3. Microhardness test

We started to evaluate the scanning electron beam microscope to assess microhardness of films after indenting them with a fine diamond tool under a known load. We can indeed see clearly indentation of the  $As_2S_3$  film when only a force of 1 gm is applied to our diamond indenter (Fig. 28a). Under stronger loading (25 gm) the film starts to tear (Fig. 28b) and the substrate eventually becomes indented (Fig. 28c). Although these are only initial measurements, the technique is promising thus far, and further experiments will be undertaken to quantify the results and compare them with "standard eraser rub" or standard cheesecloth tests.

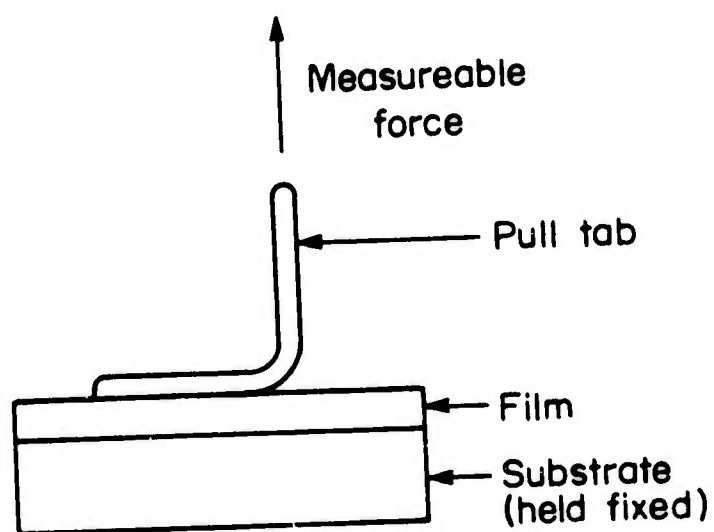
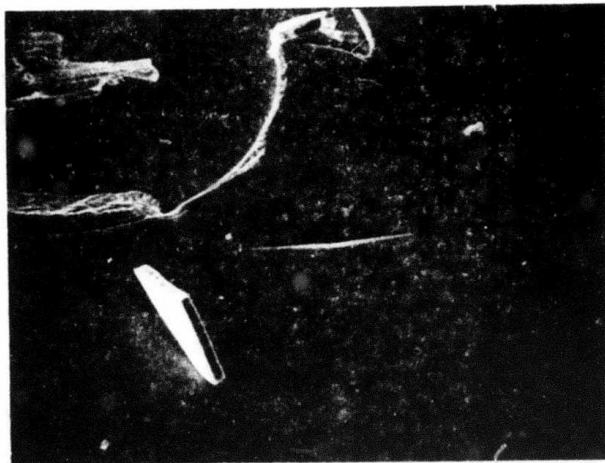


Fig. 27 Film Adhesion Experiment, Pull Tab Method.





PBN-74-807

1 gm load



26 gm load



51 gm load

Fig. 28 Microhardness Test of  $\text{As}_2\text{S}_3$  Film ( $2.7 \mu\text{m}$  thick) on  $\text{BaF}_2$  Substrate using the Scanning Electron Microscope.  $700\times$ .

### III. FUTURE WORK

During December we expect to receive the  $\text{BaF}_2$  and  $\text{ZnSe}$  ATR plates coated with  $\text{ZnSe}$ ,  $\text{ZnS}$ ,  $\text{As}_2\text{S}_3$  and  $\text{ThF}_4$ . Absorption measurements using optical and calorimetric techniques will begin as soon as the samples are in hand.

We have recommended to MICOM that we also investigate ATR plates made of  $\text{SrF}_2$ . This material is currently being cast in our laboratory and it appears to be one of the strongest contenders for high-power laser windows at  $3.8\mu\text{m}$ . If MICOM concurs with this recommendation, we will coat  $\text{SrF}_2$  with materials showing the greatest promise for windows in this frequency range.

Our initial measurements on ATR plates show that it will be difficult to determine optical absorption from optical measurements alone. Calorimetric measurements appear to be much more promising. In order to obtain a reasonably accurate absorption coefficient for the film, very thin, low-absorption substrates will be used so that the absorption of the film becomes comparable to that of the substrate. The calorimetric measurements will be carried out using Raytheon's CO laser, and, where applicable, its  $\text{CO}_2$  laser. If promising, the absorption will also be determined with a DF laser at Government-furnished facilities, if available.

For the mechanical evaluation of films we will continue to investigate pull and peel tests on surface coatings to determine adhesion. To evaluate microhardness, we will use the scanning electron beam microscope to study indentations made by a diamond tool into the surface coating alone. Initial experiments show promise for this technique.

Optimum polishing techniques will be evaluated for  $\text{BaF}_2$ . We have recommended that no further work be done on  $\text{ZnSe}$  surfaces since both Raytheon and other laboratories have learned to prepare  $\text{ZnSe}$  surfaces such that laser damage is not due to the surface. Because of the emerging importance of  $\text{SrF}_2$ , we recommend the development of optimum polishing and surface preparation techniques for this material.

We plan to supply six 2 in. by 1/2 in.  $\text{SrF}_2$  (or  $\text{CaF}_2$ ) windows for testing at MICOM. These windows will be optimally prepared to determine their actual usefulness as high-power laser windows at  $3.8 \mu\text{m}$ .

We have also recommended that no further work be done on the absorption band of KCl near  $10 \mu\text{m}$ . More recent work at the Naval Electronics Laboratory and the Naval Research Laboratory has shown that this absorption band can be controlled so that it no longer seriously interferes with the use of KCl for laser windows at  $10.6 \mu\text{m}$ .

Finally, we recommended that no further work be done on low-loss cooling liquids. No low-loss liquids were identified in the literature search. Furthermore, there are theoretical reasons for believing that organic liquids cannot be made with low enough absorption coefficient to be useful for cooling windows.

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# BIBLIOGRAPHY: INFRARED SPECTRA OF LIQUIDS POSSIBLY SUITABLE FOR USE AS COOLANTS FOR HIGH POWER LASER WINDOWS

**1647. Infra-red Absorption Spectra of Alcohols.** J. Lecomte (Comptes Rendus, 180, pp. 825-827, March 16, 1925.)—For measurements in the region  $2.75\mu$  to  $8\mu$ , a fluorite prism has been used for which the dispersion warrants an accuracy of  $0.01\mu$ . All the alcohols studied show strong absorption at  $3\mu$  to  $3.5\mu$  and  $6.85\mu$  to  $8\mu$ . There is feeble absorption between  $3.5\mu$  and  $6.85\mu$  except in a few cases in which there is strong absorption between  $5.80\mu$  and  $6.15\mu$ . The results are summarised in a table. F. S.

**733. Change in the Infra-red Absorption Spectrum of Water with Temperature.** J. R. Collins. (Phys. Rev. 26 pp. 771-779, Dec., 1925.)—By the use of two constant deviation spectrometers in series and a Coblentz linear thermopile, the absorption coefficient of water was measured for various temperatures from  $0^\circ$  to  $95^\circ\text{C}$ . The bands found showed maximum absorption at the following wave-lengths:—

At $0^\circ\text{C}$ :	0.775	—	0.985	1.21	1.45	1.96 $\mu$
At $95^\circ\text{C}$ :	0.74	0.845	0.97	1.17	1.43	1.94 $\mu$

There is a shift toward shorter wave-lengths as the temperature increases and also a marked increase in magnitude of the maximum absorption for the bands at 0.77, 0.98, and  $1.21\mu$ . These changes are qualitatively explained by Röntgen's hypothesis that water is a mixture of at least two kinds of molecules, presumably  $(\text{H}_2\text{O})_2$  and  $(\text{H}_2\text{O})_3$ , whose relative amounts change with a change of temperature. AUTHOR.

**1871. Absorption Spectra of Certain Organic Liquids in the Near Infra-Red.** J. W. Sappenfield. Phys. Rev. 51, pp. 37-47, Jan., 1929.

Absorption spectra have been studied in the region from  $0.8$  to  $2.5\mu$  with an accuracy of  $0.002\mu$  for twenty-four organic liquids, including nine alcohols, six esters, two ethers, two aldehydes, and five miscellaneous compounds. The carbon-hydrogen linkage and other similar ones have been discussed as a probable source of the absorption. While certain inconsistencies are pointed out, no other explanation is available. The relative intensity of the various bands has been discussed, and it is shown that the bands at  $1.4$  and  $1.0\mu$  and the two bands at  $1.2$  and  $0.9\mu$  evidently arise from different sources. The effect of homology is shown to be slight, which agrees with the conclusions of Weniger [see Abstract 94 (1911)]. An attempt has been made to get a relation between different band heads of a particular compound. The anharmonic series as suggested by Ellis, and the relation  $\nu_n = \nu_0(n)^{1/2}$  suggested by Gapon were both used with moderate success. The latter equation was modified so as to read  $\nu_n = \nu_0/(n)^{1/2}$  and applied to part of the data of Weniger with moderate success. AUTHOR.

**2835. Infra-Red Absorption of Water from  $2.5\mu$  to  $6.5\mu$ .** E. K. Plyler and C. J. Craven. J. Chem. Phys. 2, pp. 303-305, June, 1934.—A study has been made of the infra-red absorption bands of water from  $2.5\mu$  to  $6.5\mu$  and new bands have been found at  $3.30\mu$ ,  $5.56\mu$  and  $5.83\mu$ . The band at  $4.7\mu$  showed an irregular envelope and may contain several components. The  $3\mu$  band showed a shift with thickness and is probably made up of four components. The change in position of the maximum in the  $3\mu$  region with thickness is explained as due to difference in sharpness of the components which constitute the band. The band at  $6.15\mu$  did not show the corresponding shift with thickness. AUTHORS.

**4204. Infra-Red Absorption Spectrum of Water Containing Deuterium.** J. W. Ellis and B. W. Sorge. *J. Chem. Phys.* 2. pp. 552-564, Sept., 1934.—Absorption percentages for the region 1-10 $\mu$  are presented for one sample of water, 60 % of whose hydrogen is deuterium, and for a second sample containing 99.5 % deuterium oxide. Maxima are picked out as the three fundamental frequencies for the molecules DOD and HOD. These are compared with values predicted by an isotopic shift calculation based on data chosen from the spectrum of ordinary water. All other higher frequency maxima are interpreted as overtones or combination bands, but only after a fourth fundamental frequency is chosen in the examples of HOH and DOD. Authors.

**5041. Infra-Red Absorption Spectrum of Heavy Water.** T. Shidcl. *Phys. Math. Soc., Japan, Proc.* 10. pp. 362-364, Oct., 1934. *In English.*—The absorption of heavy water has been studied in a Kell and Zonen auto-recording glass spectrometer. Cells with glass windows were used to hold the water and the thickness of the absorbing layer was 0.3 mm. When heavy water replaced distilled water the bands of the latter at 1.98 $\mu$ , 1.46 $\mu$  and 1.18 $\mu$  were reduced considerably, and new bands appeared at 2.11 $\mu$ , 1.64 $\mu$  and 1.32 $\mu$  (faintly). Three fundamental frequencies were estimated, viz.,  $\delta(\pi)$ , 6.8 $\mu$  (1470  $\text{cm}^{-1}$ );  $\nu(\pi)$ , 3.8 $\mu$  (2623  $\text{cm}^{-1}$ );  $\nu(\sigma)$ , 2.9 $\mu$  (3477  $\text{cm}^{-1}$ ). Tables of data are included. H. H. Ho.

**5016. Infra-Red Absorption of Oxygenated Water.** A. Malone. *N. Cimento*, 12. pp. 358-360, June, 1935.—Observations are made with a registering spectrograph of the infra-red absorption spectrum of oxygenated water as far as 5.5 $\mu$ . The oxygenated water contained 36 % by weight of  $\text{H}_2\text{O}_2$  corresponding to a concentration of 12 gm. mol. of  $\text{H}_2\text{O}_2$  and 40 gm. mol. of  $\text{H}_2\text{O}$  per l. of solution. Throughout the spectral field studied an increase of absorption is found in accordance with analogous cases in processes of molecular association. There is a profound modification of the band at 3 $\mu$ , whilst the maxima at 1.5 $\mu$  and 2 $\mu$  whose frequencies are multiples of one of the three frequencies of the fundamental band at 3 $\mu$  remain practically unchanged. J. J. S.

**3656. Absorption of Water and Alcohols between 0.70-0.95 $\mu$ .** E. Ganz. *Ann. d. Physik*, 26. 4. pp. 331-348, June, 1936.—A 3-prism spectrograph was used as monochromator and a photo-cell as detector. Measurements of the variation with temperature of absorption of pure water were found to agree with Collins' results [see Abstract 733 (1926)]. The absorption-constant at the maximum is proportional to the density of the water. The difference in absorption of water singly- and doubly-distilled noted by Lange and Schusterius [see Abstract 3208 (1932)] is not confirmed. The temperature variation of absorption of the first four alcohols has also been investigated. Earlier observations of the absorption of water between 0.18 $\mu$ -2.5 $\mu$  have been collected. F. S.

**1684. Absorption Spectrum of Water between 2.5 and 6.5  $\mu$ .** E. Ganz. *Ann. d. Physik*, 28. 5. pp. 445-457, March, 1937.—Three absorption bands are studied. The thickness of the absorbing layer varies between 5 and 200  $\mu$ . In this region the absorption coefficient is not independent of the thickness, but decreases very much with increasing thickness. This is attributed to scattering, but no attempt is made to correct for the influence of scattering. The variation of the band with temperature up to 84° C. and the influence of dissolved ions are also studied. R. P.

1672. Near Infra-Red Absorption Spectrum of Heavy Water. L. Kellner. *Roy. Soc., Proc.* 159A. pp. 410-415, April 1, 1937.—An investigation of the infra-red absorption of heavy water in the region 0.8-2.1  $\mu$ . Four absorption bands due to the vibrations of the  $D_2O$  molecule are found whose positions are given in Table 1 of the original. The results are compared with previous observations. It is shown that these bands can be explained as certain overtones and combination tones of the three fundamentals in the same way as the corresponding bands of light water vapour have been interpreted by Mecke. AUTHOR.

3587. Infra-Red Absorption Spectra of  $H_2O$  Liquid, Solid and in Solution. G. Bosschleter and J. Errera. *Comptes Rendus*, 204. pp. 1719-1721, June 7, 1937.—Dilute solutions of water in  $CCl_4$  and  $CS_2$  give a similar absorption to that of water vapour, because of the absence of any hydrogen linkages. In ice and water the absorption is quite different. The bands at 3500  $cm^{-1}$ . (stronger in water) are attributed to H linkages between two or more molecules close together; the 3200 bands (stronger in ice) to a (crystal) structure of polymolecules in which each O is surrounded by 4H. H. G. C.

4056. Intermolecular Association and Infra-Red Absorption of Water. G. Bosschleter and J. Errera. *J. de Physique et le Radium*, 8 pp. 229-232, June, 1937.—The absorption of  $H_2O$  liquid, gaseous and in solution is examined at about 3 $\mu$ . A band at 3520-3700  $cm^{-1}$ . is monomolecular, being independent of the solvent. A band about 3300  $cm^{-1}$ . arises from H bonds. H. G. C.

206. Absorption Spectrum of Water. A. Carrelli. *N. Cimento*, 14. pp. 245-256, June, 1937. The infra red absorption spectrum of water is measured and for comparison the spectra of the aqueous solutions of some salts and that of gypsum containing water of crystallisation are obtained. From these results conclusions as to the classification of the absorption maxima are drawn. R. P.

4057. Near Infra-Red Absorption Band of Liquid Water at 1.79 $\mu$ . J. R. Collins. *Phys. Rev.* 52. pp. 83-90, July 15, 1937.—The near infra-red absorption band of liquid water at 1.79 $\mu$  is studied at various temperatures. No apparent changes in the band are detected in the temperature range from 4° C. to 137° C. AUTHOR.

5341. Infra-Red Absorption Spectra of  $H_2O$  Liquid, Solid and in Solution in Dioxane. G. Bosschleter and J. Errera. *Comptes Rendus*, 205. pp. 560-562, Oct. 4, 1937.—The results of previous work [see Abstracts 3587 and 4056 (1937)] are checked with new apparatus to remove the possibility of false bands due to errors in the spectroscope near the region of the absorption of quartz. The band at 3100  $cm^{-1}$ . is attributed to bonds between H atoms of different molecules, that at 3250  $cm^{-1}$ . to the bands between the H atoms in the crystal lattice in which each O is surrounded by 4H. H. G. C.

1664. New Infra-Red Absorption Band of Liquid Water at 2.52 $\mu$ . J. R. Collins. *Phys. Rev.* 55. pp. 470-472, March 1, 1939.—The absorption of liquid water in the spectral region from 2.00 to 2.65 $\mu$  was measured by means of a thermopile and glass prism spectrometer with a slit width of 100 Å in a search for a weak absorption band predicted by Ellis as a combination band occurring in liquid water but not in water vapour. A band was found with a peak at 2.52 $\mu$  and with a maximum absorption coefficient of about 34. This is the fifth absorption band to be found in the spectrum of liquid water that has no counterpart in the spectrum of water vapour. AUTHOR.

755. Absorption of water at different temperatures from 2.5 to 7.5  $\mu$ . J. J. FOX AND A. E. MARTIN. *Roy. Soc., Proc. A*, 174, pp. 231-262, Feb. 1, 1940.—The authors investigated the infra-red absorption of ice at  $-9^{\circ}\text{C}$ ., water at  $+3^{\circ}\text{C}$ ., and  $+70^{\circ}\text{C}$ ., and water dissolved in  $\text{CCl}_4$  from 2.5 to 7.5  $\mu$  with a grating spectrometer of high resolution. The 3  $\mu$  band shifts to higher frequencies with increasing temperature while the 6  $\mu$  and 4.7  $\mu$  bands move in the opposite direction. The reasons for this behaviour are hydrogen bonds between neighbouring  $\text{H}_2\text{O}$  molecules which decrease the OH valence forces and increase the angular forces. The hydrogen bonds are strongest in ice and decrease with rising temperature. The intensity of the valence vibrations shows a very marked increase with growing association of the molecules. Two valence frequencies at 3705 and 3614  $\text{cm}^{-1}$ , are found for water dissolved in  $\text{CCl}_4$ , 40-50  $\text{cm}^{-1}$  below the corresponding value for  $\text{H}_2\text{O}$  vapour. The 4.7  $\mu$  band is ascribed to the combination frequency between the deformation frequency and the frequency of hindered rotation at approximately 500  $\text{cm}^{-1}$ , which latter frequency diminishes rapidly with rising temperature and disappears altogether for the vapour in accordance with the observations on the 4.7  $\mu$  band. A brief discussion is given of the structure of liquid water and its effects on the infra-red spectrum. L. K.

Absorption of light by liquid  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  in the infra-red between 5  $\mu$  and 27  $\mu$ . SOHM, M. *Z. Phys.*, 116, 1-2, pp. 34-46, 1940.—The absorption spectra of liquid  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  are photographed with layers of several  $\mu$  thickness, starting from the range of molecular vibrations up to a wavelength of 27  $\mu$ . A group of nearly equidistant absorption lines was observed beginning at 14  $\mu$  and 19  $\mu$  for  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  respectively. o. o.

5274. The near infrared absorption spectrum of liquid water. J. A. CURCIO AND C. C. PETTY. *J. Opt. Soc. Amer.*, 41, 302-4 (May, 1951).

The near i.r. absorption spectrum of liquid water at  $20^{\circ}\text{C}$  has been reinvestigated using a PbS cell detector system. The total spectral range investigated was from 0.70 to 2.50  $\mu$ . A curve is included which shows 5 prominent absorption bands at 0.76, 0.97, 1.19, 1.45 and 1.94  $\mu$ ; and a table gives experimental results of water absorption at  $20^{\circ}\text{C}$ . A.

5026. Transmission of water in the near infrared. L. GENZL. *Optik*, 9, 143 (No. 3, 1952) *In German*.

Data of Curcio and Petty [Abstr. 5274 (1951)] are used to plot transmissions for thicknesses 0.01-10 cm and wavelengths 0.7-2.5  $\mu$ . G. P. LOTHIAN

1517. The molecular spectra of condensed oxygen and the  $\text{O}_4$  molecule. A. L. SMITH AND H. L. JOHNSTON. Letter in *J. chem. Phys.*, 20, 1972-3 (Dec., 1952).

The i.r. and Raman spectra of liquid and solid oxygen and liquid oxygen-nitrogen mixtures are discussed. For the i.r. spectra, the curves of absorption coefficient v. frequency of vibration exhibit an anomaly which is attributed to the presence of  $\text{O}_4$  molecules. G. I. W. LLEWELLYN



4366. Infrared absorption spectrum of liquid water in the 3200 to 3600  $\text{cm}^{-1}$  region. S. N. ANDRIEV AND T. G. BAICHEVA. *Dokl. Akad. Nauk SSSR*, 90, No. 2, 149-51 (1953) *In Russian*. English translation, *U.S. National Sci. Found. NSF-tr-66*.

The results obtained are represented graphically, and discussed with particular reference to previously recorded data. G. I. W. LLEWELLYNS

10640. Infrared absorption of liquid water from 2 to 42 microns. E. K. PLYLER AND N. ACQUISTA. Letter in *J. Opt. Soc. Amer.*, 44, 505 (June, 1954).

In order to investigate how long-wave radiation is transmitted through water in animal tissue at body temperature, the spectrum of water layers of thickness 0.005, 0.01, and 0.03 mm was taken in this region. The transmission graphs are reproduced. One broad band at  $15.5 \mu$  does not appear in the vapour spectrum and is attributed to intermolecular vibrations. A. J. TAYLOR

6005. Infrared absorption of liquid and solid hydrogen. E. J. ALLIN, W. F. J. HARE AND R. E. MACDONALD. Letter in *Phys. Rev.*, 98, No. 2, 554-5 (April 15, 1955).

Comparison with gaseous  $\text{H}_2$  at 3400 atm in the range 4000-5500  $\text{cm}^{-1}$  and assignment of the peaks. G. F. LOTHIAN

7847. Infrared spectra of liquid anhydrous hydrogen fluoride, liquid sulfur dioxide, and hydrogen fluoride-sulfur dioxide solutions. R. H. MAYBURY, S. GORDON AND J. J. KATZ. *J. chem. Phys.*, 23, No. 7, 1277-81 (July, 1955).

The infrared spectra of anhydrous liquid hydrogen fluoride, anhydrous liquid sulphur dioxide and mixtures of the two have been measured in the region from 1 to  $25 \mu$ . A value for the extinction coefficient for the polymer peak in the region higher than previously reported has been found, reflecting the existence of a greater proportion of higher hydrogen fluoride polymers in the liquid as compared with the gas. A study of the change in the spectra of solutions of varying concentration of anhydrous liquid hydrogen fluoride in anhydrous liquid sulphur dioxide has been made and its possible relation to the structure of the polymers in liquid hydrogen fluoride examined. The possible applicability of obtaining spectra of protein dissolved in anhydrous liquid mixtures of hydrogen fluoride and sulphur dioxide has been explored and a spectrum of silk fibroin in this solvent is presented. A.

## 229. INFRARED ABSORPTION OF LIQUID AND SOLID HYDROGEN WITH VARIOUS ORTHO-PARA RATIOS.

W. F. J. Hare, E. J. Allin and H. L. Welsh. *Phys. Rev.*, Vol. 99, No. 6, 1887-8 (Sept. 15, 1955).

The band covering 4000-5500  $\text{cm}^{-1}$  is shown for 25-100% para- $\text{H}_2$ . It is concluded that  $Q_Q$ ,  $S_1(0)$  and  $S_1(1)$  components for pure p- $\text{H}_2$  arise from quadrupole interaction, since their relative intensities accord with theoretical values for these interactions; but this agreement is no longer found in ortho-para mixtures. G. F. Lothian

1071. ABSORPTION BANDS OF  $\text{CCl}_4$  IN THE FAR INFRARED REGION. H. Yoshinaga.  
J. chem. Phys., Vol. 23, No. 11, 2206 (Nov., 1955).

New measurements of liquid  $\text{CCl}_4$ -bands from 660 to  $100 \text{ cm}^{-1}$  are shown in absorption curves for 3 thicknesses of cell and a table of maxima with their assignments is given. These agree with Raman data. C. Turner

967. ON THE STRUCTURE OF ABSORPTION BANDS OF LIQUID  $\text{H}_2\text{O}$ ,  $\text{D}_2\text{O}$  AND  $\text{HDO}$ , DETERMINED BY THEIR MOLECULAR STRUCTURE. M.O. Bulanin.  
Optika i Spektrosk., Vol. 2, No. 5, 557-61 (1957). In Russian.

The spectra were examined on an instrument with an LiF prism; the  $\text{H}_2\text{O}$  spectra were also measured on a grating spectrometer. The  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  gave a doublet structure with absorption maxima at  $3425$ ,  $3250$  and  $2550$ ,  $2435 \text{ cm}^{-1}$  respectively. The  $\text{HDO}$  gave broad bands with maxima at  $3420$  and  $2510 \text{ cm}^{-1}$ . The results are used in a discussion on the theoretical structure of these liquids. L. Bovey

7965. ABSORPTION SPECTRUM OF LIQUID OXYGEN IN THE TEMPERATURE RANGE  $77$ - $153^\circ \text{K}$  ( $12600$ - $3300 \text{ \AA}$ ). V.I. Dianov-Klovov.

Optika i Spektrosk., Vol. 4, No. 4, 448-54 (April, 1958). In Russian. English summary: PB 141047T-9, obtainable from Office of Technical Services, U.S. Dept. of Commerce, Washington, D.C., U.S.A.

The extinction coefficient  $\epsilon_m$  was measured at the band maxima and integral absorption coefficients found for the  $12600$  and  $10600 \text{ \AA}$  bands. The change of  $\epsilon_m \rho$  with temperature, where  $\rho$  is the density of the liquid, is similar for the five Ellis-Kneser groups,  $^2\Sigma - ^1\Delta$ ,  $^2\Sigma - ^1\Sigma$ ,  $2^2\Sigma - 2^1\Delta$ ,  $2^2\Sigma - (^1\Delta + ^1\Sigma)$ ,  $2^2\Sigma - 2^1\Sigma$ , and is also similar to the change of  $\rho$  with temperature. Results are given for determination of  $\epsilon_m$  in the liquid diluted with  $\text{N}_2$  at  $78^\circ \text{K}$ , whereby the oxygen spectrum is generally weakened. Temperature change affects various groups of bands differently in dilution. It is suggested that the absorption spectrum is due to the complex  $(\text{O}_2)_2$  in liquid or compressed oxygen. S.T. Henderson

#### 82. ABSORPTION OF RADIATION IN LIQUID WATER.

E.I. Bocharov and A.S. Krutikov.

Izv. Akad. Nauk SSSR, Ser. geofiz., 1958, No. 7, 923-6. In Russian. English summary: PB 141042T-3, obtainable from Office of Technical Services, U.S. Dept. of Commerce, Washington, D.C., U.S.A.

The authors remeasured the absorption bands in the spectrum of liquid water in the  $2600$  -  $7000 \text{ cm}^{-1}$  region using LiF and NaCl prisms. The positions and the absorption coefficients of the observed bands are compared with the results of other workers. A variable-length absorption cell capable of giving very thin samples ( $0.4 \text{ microns}$ ), is also described. D.L. Greenaway

5725. THE INFRARED SPECTRUM OF LIQUID AND SOLID HYDROGEN. E.J. Allin, H.P. Gush, W.F.J. Hare and H.L. Welsh. Nuovo Cimento Suppl., Vol. 9, No. 1, 77-83 (1958).

Infrared spectra of liquid and solid hydrogen over the range  $4100$ - $5500 \text{ cm}^{-1}$  were obtained using a high resolution grating spectrometer, and a considerable amount of new detail observed. A small but abrupt change has been detected at the fusion point, but the similarity of spectra of solid and liquid indicates short range order in the liquid, very similar to that in the solid, just above the fusion point. Certain features of the S lines in the fundamental band of the solid are ascribed to double transitions, in which one molecule performs the vibrational transition and a second performs simultaneously a rotational transition in its ground vibrational state. The predominance of these transitions is discussed with reference to the theory of induced absorption in dense gases. The effect of altering the ortho-para ratio of solid hydrogen has also been investigated and the observed changes in spectral intensity distribution correlated with the molecular arrangement. D.L. Greenaway

9426. ON THE ORIGIN OF THE SPECTRUM OF LIQUID AND COMPRESSED OXYGEN (12 600-3000 Å). V.I. Dianov-Klovkov. Optika i Spektrosk., Vol. 6, No. 4, 457-62 (April, 1959). In Russian.

To explain the origin of the absorption spectrum of condensed oxygen in the region 12 600-3000 Å it is necessary to decide whether the spectrum is due to a pair of interacting molecules ( $O_2$ )<sub>2</sub> or to one molecule  $O_2$ . To answer this question, the author investigated the temperature and density dependences of the intensity of absorption bands of condensed oxygen. The results obtained agree with the assumption that the absorption spectrum of condensed oxygen in the region 12 600-3000 Å is almost entirely due to the dipole transitions in "statistical" complexes ( $O_2$ )<sub>2</sub>. A. Tybulewicz.

4196 THE INFRARED FUNDAMENTAL BAND OF LIQUID AND SOLID HYDROGEN.

H.P. Gush, W.F.J. Harc, E.J. Allin and H.L. Welsh. Canad. J. Phys., Vol. 38, No. 2, 176-93 (Feb., 1960).

The infrared fundamental band of liquid and solid hydrogen was investigated over a range of para-concentrations from 25% to 100% with a prism spectrometer and, in part, with a grating spectrometer at a resolution of  $\sim 0.2 \text{ cm}^{-1}$ . The spectrum of the solid shows (a) comparatively sharp Q, S(0), and S(1) lines due to quadrupolar interaction, (b) broad bands interpreted as combination tones of the molecular frequencies with the lattice frequencies (phonon spectra), and (c) weak double transitions of the type  $S_1(0) + S_0(0)$ . At high resolution the quadrupolar S(0) and S(1) groups show weak single transitions,  $S_1(0)$  and  $S_1(1)$ , and much stronger double transitions of the type  $Q_1(J) + S_0(1)$ ,  $J = 0, 1$ . In solid parahydrogen the lines become very sharp and the double transition,  $Q_1(0) + S_0(0)$ , shows a complex structure; the observations are in good agreement with the theory of the rotational and vibrational levels of solid parahydrogen by Van Kranendonk. The quadrupolar Q branch shows a structure which is interpreted as double transitions of the type  $Q \pm \delta_1$ , where the  $\delta_1$  are the small changes in energy due to the orientational transitions of two ortho-molecules. The phonon spectra show a maximum at the Debye temperature of the solid, and, at higher resolution, a structure indicative of the various branches of the lattice frequencies. A long extension of the phonon spectrum towards high frequencies is probably due to multiple phonon creation. Double transitions, for which the cancellation principle in induced absorption does not apply, account for at least 98% of the intensity of the spectrum of the solid.

6860 INFRARED SPECTRA OF WATER. R. Mecke.

Current Sci. (India), Vol. 30, No. 2, 43-4 (Feb., 1961).

Dilution of  $H_2O$ ,  $D_2O$  and HDO in  $SbCl_3$  eliminates effects of hydrogen bonding. Vibration bands are sharp and the stretching vibrations of HDO coincide with those of  $H_2O$  and  $D_2O$ , indicating that "there is no great interaction between the vibrations of the HO and DO valence bonds". Splitting of the bending vibration at  $1600 \text{ cm}^{-1}$  suggests O-bonding to Sb. G.F. Lothian.

15882 LOW-FREQUENCY INFRARED ABSORPTION SPECTRUM OF THE HYDROGEN BOND IN LIQUID WATER AND IN CRYSTAL HYDRATES. A.E. Stanevich and N.G. Yaroslavskii. Dokl. Akad. Nauk SSSR, Vol. 137, No. 1, 60-3 (March 1, 1961). In Russian.

The structure of a broad infrared absorption band of light and heavy water is discussed. Besides frequencies found experimentally a number of frequencies calculated for the possible vibrational energies of molecular bonds are also given. The latter contribute to the general shape of the broad band. The absorption spectra of a number of compounds containing water of crystallization were investigated. It was found that the bands disappear when the compound is heated to a high temperature. This is explained by attributing the discrete absorption bands to the water molecules weakly bound to the crystalline structure of the compound. A table of frequencies of the absorption bands for all compounds examined is given, but no interpretation is attempted due to the complexity of the vibrational states of these molecules. [English translation in: Soviet Physics-Doklady (USA), Vol. 6, No. 3, 224-7 (Sept., 1961)].

W.G. Jordan

11026 ABSORPTION CROSS-SECTIONS OF WATER DROPS  
FOR INFRARED RADIATION.

J.J. Stephens and J.R. Gerhardt.

J. Meteorol. (USA), Vol. 18, No. 6, 818-22 (Dec., 1961).

Tables are given showing the absorption cross-section at 9 wavelengths in the maximum emission region (5-18 $\mu$ ) of the terrestrial spectrum. The results are for a series of drop diameters up to 30 $\mu$ . It is shown that the ability of a given drop size to absorb is heavily dependent on the imaginary part of the refractive index.

D.L. Greenaway

11027 SPECTRALLY AVERAGED TOTAL ATTENUATION,  
SCATTERING, AND ABSORPTION CROSS-SECTIONS  
FOR INFRARED RADIATION. J.J. Stephens.

J. Meteorol. (USA), Vol. 18, No. 6, 822-8 (Dec., 1961).

Tables are given showing the total attenuation, scattering, and absorption cross-sections of water drops with diameters between 1 and 10 $\mu$  for 10 temperatures (253°-298° K). The results are all averaged over the wavelength range 4-90 $\mu$  (which includes approximately 99% of the terrestrial spectral energy), and provide a means of formulating a comprehensive energy budget for radiation fog.

D.L. Greenaway

1693 INFRARED SPECTRA OF LIQUID AND SOLID CARBON  
MONOXIDE. G.E. Fwing.

J. chem. Phys. (USA), Vol. 37, No. 10, 2550-6 (Nov. 15, 1962).

A low-temperature cell suitable for the study of the infrared spectra of pure liquids in the fundamental region is described. Selection rules are derived based on the assumption that diatomic molecules in the liquid state can undergo hindered rotation. The infrared absorption band shape is predicted to resemble the P- and R- branch envelope of the gas phase molecule in the wings, but to have an intense Q branch at the band centre. The observed spectra of carbon monoxide as a liquid is in reasonable agreement with these selection rules. It is concluded that a considerable fraction of molecules in the liquid state can undergo nearly free rotation. The spectrum of carbon monoxide just below its freezing point suggests, however, that the rotatory motion of the molecules in the solid can best be described as librational.

153 NEAR-INFRARED STUDIES OF THE STRUCTURE OF  
WATER. 1. PURE WATER. K. Buijs and G. R. Choppin.

J. Chem. Phys. (USA), Vol. 39, No. 8, 2035-41 (15 Oct. 1963).

The absorption bands of water in the 1.1-1.3 $\mu$  region were measured. From the extinction coefficients, concentrations of water species involving 2, 1, and 0 hydrogen bonds per molecule were calculated. The temperature dependence of these concentrations yielded a value of 3.7-4.5 kcal for the energy involved in breaking one mole of hydrogen bonds in water. On melting, 46% of the hydrogen bonds originally present in ice are broken; by 72°C the percentage broken has increased to 61. The results were used in conjunction with the flickering cluster model of Frank and Wen to obtain an upper limit for the average size of the water polymers of 90 molecules of H<sub>2</sub>O at 20°C.

11109 THE ABSORPTION SPECTRA OF LIQUID PHASE H<sub>2</sub>O, HDO  
AND D<sub>2</sub>O FROM 0.7 $\mu$  TO 10 $\mu$ .

J. G. Bayly, V. B. Kartha and W. H. Stevens.

Infrared Phys. (GB), Vol. 3, No. 4, 211-22 (Dec. 1963).

The H<sub>2</sub>O spectrum is based on that of natural water, the D<sub>2</sub>O spectrum on that of heavy water containing approximately 99.6 weight per cent D<sub>2</sub>O. The HDO spectrum has been deduced from spectra of H<sub>2</sub>O-HDO-D<sub>2</sub>O mixtures by application of Beer's law. The spectra are presented in terms of logarithms of both an extinction length, L, the sample thickness that has unit optical density, and a molecular extinction coefficient,  $\epsilon$ , plotted against logarithms of both wavelength and wave number. Vibration mode assignments have been made for most of the absorption bands observed. The spectral data obtained have been useful in the development of infrared monitoring instrumentation and methods of analysis for H<sub>2</sub>O-HDO-D<sub>2</sub>O mixtures in connection with the heavy water reactor research programs at the Chalk River Nuclear Laboratories.

**21138 TRANSMISSION OF INFRARED RADIATION THROUGH LIQUID WATER AND THROUGH WATER VAPOR NEAR SATURATION.** R. Goldstein and S. S. Penner.  
J. Quant. Spectrosc. Radiative Transfer (GB), Vol. 4, No. 2, 359-61 (March-April 1964).

The noticeable differences between the i.r. spectrum of liquid water and that of water vapor near saturation indicates that the molecular aggregates in the two states are significantly different. It is also noted that as liquid water is heated its absorption spectrum approaches that of water vapor. C. R. Ward

**21139 ON THE SPECTRUM AND STRUCTURE OF WATER AND IONIC SOLUTIONS.** D. F. Hornig.  
J. Chem. Phys. (USA), Vol. 40, No. 10, 3119-20 (15 May 1964).

It is suggested that the H<sub>2</sub>O bands near 8000 cm<sup>-1</sup> may be combination vibrations, and that there is no evidence for their arising from hydrogen bonded polymers as suggested by Buijs and Choppin (Abstr. 153, 154 of 1964). G. F. Lothian

**21140 ASSIGNMENT OF THE NEAR-INFRARED BANDS OF WATER AND IONIC SOLUTIONS.**

K. Buijs and G. R. Choppin.  
J. Chem. Phys. (USA), Vol. 40, No. 10, 3120 (15 May 1964).

The authors reaffirm their earlier conclusions (Abstr. 153, 154 of 1964) that the bands around 8000 cm<sup>-1</sup> are due to hydrogen bonded polymers, in contradiction to the suggestions of Hornig. Their conclusions are based mainly on intensity considerations. G. F. Lothian

**21137 THE NEAR-INFRARED ABSORPTION OF LIQUID WATER AT TEMPERATURES BETWEEN 27 AND 209°C.**

R. Goldstein and S. S. Penner.  
J. Quant. Spectrosc. Radiative Transfer (GB), Vol. 4, No. 3, 441-51 (May-June 1964).

The spectral absorption coefficients of liquid water were measured between 2200 and 3000 cm<sup>-1</sup> and between 3700 and 7600 cm<sup>-1</sup> at temperatures of 27, 89, 159, and 209°C. The integrated intensities for the entire spectral regions extending from 4600 to 5900 cm<sup>-1</sup> and from 5900 to 7600 cm<sup>-1</sup> were also determined at each of the specified temperatures. Following Buijs and Choppin (1963), the experimental data have been used, in a highly simplified analysis, for the determination of hydrogen bonding in liquid water on the assumption that water consists of clusters containing only zero, one or two hydrogen bonds per molecule. A more complete analysis of the experimental measurements is briefly indicated, in which the full range of results on spectral absorption coefficients as a continuous function of frequency is properly utilized.

**1191 A STUDY OF THE INFRARED SPECTRA OF LIQUID OXYGEN AND NITROGEN.**

M. O. Bulanin and Yu. V. Peterson.  
Optika i Spektrosk. (USSR), Vol. 16, No. 6, 987-91 (June 1964).  
In Russian. English translation in: Optics and Spectrosc. (USA), Vol. 16, No. 6, 533-5 (June 1964).

The infrared absorption spectra of technical liquid oxygen and nitrogen have been obtained in the region 3500-1200 cm<sup>-1</sup>, and a complete interpretation of them is given. It is shown that solutions of acetylene in liquid oxygen have a complex structure, and possible explanations of the observed phenomena are examined.



30455 RELATIONSHIP BETWEEN THE OBSERVED AND TRUE ABSORPTION SPECTRA OF MOLECULES IN A CONDENSED MEDIUM. IV. INTENSE INFRARED ABSORPTION BANDS IN LIQUID CHLOROFORM AND CARBON TETRACHLORIDE ( $740-810\text{ cm}^{-1}$ ). V. S. Libov, N. G. Bakhshiev and O. P. Girin. *Optika i Spektrosk. (USSR)*, Vol. 16, No. 6, 1016-23 (June 1964). In Russian. English translation in: *Optics and Spectrosc. (USA)*, Vol. 16, No. 6, 549-52 (June 1964).

For Pt III see Abstr. 3831 of 1964. The true absorption spectra  $B(\nu)$  of  $\text{CHCl}_3$  and  $\text{CCl}_4$  in the liquid phase were determined in the region of bands corresponding to antisymmetric valence vibrations of C-Cl ( $740-810\text{ cm}^{-1}$ ). It was established that the true absorption spectra differed from the observed spectra  $K(\nu)$  in all characteristics and were very close to the spectra of the gaseous phase. It was shown that in the general case, conclusions concerning the spectroscopic properties of molecules in a condensed medium based on analysis of observed spectra  $K(\nu)$  are not correct. It was noted that some difficulties and contradictions which appear in attempts to interpret a number of phenomena connected with the effect of intermolecular interactions on the spectra can be eliminated to a certain extent by converting from observed to true absorption spectra.

6188 NEAR INFRARED SPECTRA OF WATER AND AQUEOUS SOLUTIONS. H. Yamatera, B. Fitzpatrick and G. Gordon. *J. Molecular Spectrosc. (USA)*, Vol. 14, No. 3, 268-78 (Nov. 1964).

Spectra ranging from  $4000$  to  $12500\text{ cm}^{-1}$  were obtained with  $\text{H}_2\text{O}$ ,  $\text{D}_2\text{O}$ ,  $\text{D}_2\text{O}-\text{H}_2\text{O}$  mixtures, and solutions of these solvents containing various ionic species. The shapes and/or positions of these bands were influenced by both temperature and dissolved salts. In the  $8300\text{-cm}^{-1}$  region, a pronounced band was observed at  $8640\text{ cm}^{-1}$  with  $\text{H}_2\text{O}$  near the boiling point, whereas with ice a broad but rather well-formed band was observed at  $7990\text{ cm}^{-1}$ . In  $\text{H}_2\text{O}$  at room temperature or below a very broad and deformed band appeared at  $8310\text{ cm}^{-1}$  with a distinct shoulder around  $8600\text{ cm}^{-1}$ , which became more apparent with an increase in temperature. The effect of dissolved species on the spectrum of  $\text{H}_2\text{O}$  was very similar to the observed temperature effect, and the relative intensity of the absorption at  $8640\text{ cm}^{-1}$  and at  $8310\text{ cm}^{-1}$  seems to be indicative of the degree of "structure-breaking" or "structure-making" power of the dissolved species. The order of increasing structure-breaking (or decreasing structure-making) power deduced from the spectra was  $\text{Cl}^- < \text{Br}^- < \text{I}^- < \text{ClO}_4^-$  and  $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Cs}^+ < \text{N}(\text{CH}_3)_4^+$ . This is in good agreement with the published results from measurement of other properties of solutions. Similar temperature and salt effects were also observed with other bands of  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$ .

11526 A NEAR-INFRARED STUDY OF HYDROGEN BONDING IN WATER AND DEUTERIUM OXIDE.

M. R. Thomas, H. A. Scheraga and E. E. Schrier. *J. Phys. Chem. (USA)*, Vol. 69, No. 11, 3722-6 (Nov. 1965).

The spectra of liquid  $\text{H}_2\text{O}$ , liquid  $\text{D}_2\text{O}$ ,  $\text{H}_2\text{O}$  ice, and  $\text{D}_2\text{O}$  ice were obtained in the  $1.16-1.25\text{ }\mu$  region for  $\text{H}_2\text{O}$  and the  $1.56-1.69\text{ }\mu$  region for  $\text{D}_2\text{O}$ . The temperature dependence of the liquid spectra and the extinction coefficients for the solids were utilized to calculate the concentrations of the unbonded, singly hydrogen-bonded, and doubly hydrogen-bonded water molecules as a function of temperature for liquid  $\text{H}_2\text{O}$  and for liquid  $\text{D}_2\text{O}$ . The fraction of possible hydrogen bonds remaining intact at various temperatures for  $\text{H}_2\text{O}$  compares well with previous experimental and theoretical results. The results for  $\text{D}_2\text{O}$  are consistent with the calculations of Némethy and Scheraga (1964).

7777 FAR INFRARED ABSORPTION IN LIQUID NITROGEN. N. W. B. Stone and D. Williams.

*Molecular Phys. (GB)*, Vol. 10, No. 1, 85-6 (Nov. 1965).

The present study is concerned with the far infra-red spectrum of liquid nitrogen. In view of the observed width of the vibration bands of liquid nitrogen and oxygen and the Raman evidence of quantized rotation in liquid hydrogen, it was considered possible that liquid nitrogen and oxygen might exhibit rotational absorption in the far infra-red. The present work has shown that both liquid nitrogen and liquid oxygen absorb in the spectral region between  $30\text{ cm}^{-1}$  and  $200\text{ cm}^{-1}$ ; nitrogen absorbs more strongly than oxygen.

11580 INFRARED ABSORPTION SPECTRUM OF LIQUID BORON TRIFLUORIDE.

R. G. Steinhardt, Jr., G. E. S. Fetsch and M. W. Jordan.  
J. Chem. Phys. (USA), Vol. 43, No. 12, 4528-30 (15 Dec. 1965).

17688 INFRARED ABSORPTION SPECTRUM OF CARBON SUB-SULPHIDE IN THE LIQUID STATE.

A. O. Diallo,  
C. R. Acad. Sci. (France), Vol. 261, No. 25, 5386-9 (20 Dec. 1965).  
In French.

A qualitative study is made at weak resolution, between 2 and 15  $\mu$ , of liquid carbon sub-sulphide ( $C_3S_2$ ) prepared by reduction of carbon sulphide. The vibration bands are compared with those of carbon sub-oxide ( $C_3O_2$ ). G. E. Rhead

11583 FAR-INFRARED SPECTRUM OF LIQUID WATER.

D. A. Draegert, N. W. B. Stone, B. Curnutte and D. Williams.  
J. Opt. Soc. Amer., Vol. 56, No. 1, 64-9 (Jan. 1966).

The infrared spectra of  $H_2O$  and  $D_2O$  in the liquid state at ambient temperature (30°C) have been re-mapped in the spectral region between 10 and 330  $\mu$ . The major features observed were extremely intense absorption bands with maxima at 685 and 505  $cm^{-1}$  in  $H_2O$  and  $D_2O$ , respectively. These major bands are overlapped at the low frequency ends by much less intense bands producing transmittance minima at 193 and 187  $cm^{-1}$ , respectively. No evidence was obtained for the series of narrow bands recently reported by Stanevich and Yaroslavskii (1961). Extinction coefficients have been determined for the range 170-50  $cm^{-1}$  and are compared with recent data; present data on linear absorption coefficients for  $H_2O$  in the range 1500-1100  $cm^{-1}$  are in fair agreement with the results of previous workers. The influence of temperature variations on the frequencies of infrared bands has been studied for all bands in the region between 1000 and 32  $cm^{-1}$ . Theoretical interpretation of the results is discussed briefly.

20608 FREQUENCY ASSIGNMENTS IN INFRA-RED SPECTRUM OF WATER. D. Williams.

Nature (GB), Vol. 210, 194-5 (9 April 1966).

26810 VIBRATIONAL SPECTRUM OF HYDRAZINE- $d_2$  AND A RAMAN STUDY OF HYDROGEN BONDING IN HYDRAZINE.

J. R. Durig, S. F. Bush and E. E. Mercer.  
J. Chem. Phys. (USA), Vol. 44, No. 11, 4238-47 (1 June 1966).

The infrared spectra of liquid, solid, and gaseous tetradeuterated hydrazine have been measured from 250 to 4000  $cm^{-1}$ . Fine structure was resolved for three of the perpendicular fundamental bands of the assumed symmetric top. The Raman spectra of liquid hydrazine and tetradeuterated hydrazine have been recorded and depolarization values measured. A complete vibrational analysis based on band type, position, and depolarization values is given which satisfies the product rule for both the a and b vibrational symmetry species. The intensity of the 3189- $cm^{-1}$  band of hydrazine has been studied as a function of temperature.  $\Delta H$  for H-bond formation in hydrazine is found to be -1450 cal/mole. The relative intensity of the 3189- $cm^{-1}$  band to that of the 3260- $cm^{-1}$  band has been studied as a function of concentration in dimethylsulfoxide and indicates that part of the intensity of the 3189- $cm^{-1}$  band arises from a vibrational mode of the hydrazine monomer.

2280 INFRARED AND RAMAN SPECTRA OF CARBON SUB-OXIDE IN CONDENSED PHASES.

W. H. Smith and G. E. Lerol.  
J. Chem. Phys. (USA), Vol. 45, No. 5, 1767-77 (1 Sept. 1966).

Infrared and Raman spectra of liquid, crystalline, and matrix-isolated carbon suboxide have been obtained in the region 20-4000  $cm^{-1}$ . A previously unreported solid-solid transition has been observed at  $115 \pm 5^\circ K$ , and possible structures for both crystalline phases have been inferred from the spectroscopic results. The  $\nu_2$  central-carbon bending mode  $\nu_7$  has been identified in the liquid phase at  $72 \pm 2 \text{ } cm^{-1}$ . The problem of "disappearing" sum bands is discussed, and a revised vibrational assignment and force-constant analysis for carbon suboxide is presented.

# 1154 NEAR-INFRARED SPECTRA OF H<sub>2</sub>O-D<sub>2</sub>O SOLUTIONS.

J. D. Worley and I. M. Klotz.

J. Chem. Phys. (USA), Vol. 45, No. 8, 2868-71 (15 Oct. 1966).

Near-infrared spectra have been obtained for H<sub>2</sub>O in D<sub>2</sub>O solutions containing a variety of solutes. A sharp band occurs at 1.416  $\mu$  (7062 cm<sup>-1</sup>) and other bands at 1.525 (6557 cm<sup>-1</sup>), 1.556 (6427 cm<sup>-1</sup>), and 1.666  $\mu$  (6002 cm<sup>-1</sup>). The absorbances at 1.416 and 1.556  $\mu$  increase and decrease, respectively, with increasing temperature. From this variation, a  $\Delta H^\circ$  of formation of -2.4 kcal/mole has been estimated for the O-H...O bond in these solutions. Nineteen electrolytes and one polymer, polyvinylpyrrolidone, have been examined for their effects on the spectra of water in this overtone region. No frequency shifts have been observed with added solute, only changes in absorbance. Sodium perchlorate shows the strongest structure-breaking effect. Tetraethylammonium bromide and polyvinylpyrrolidone exhibit structure-making character. A definite correlation has been found to exist between the effects of salts on the aqueous solvent and their ability to affect the conformation of a macromolecule.

# 1155 FAR-INFRARED SPECTRUM OF LIQUID WATER.

J. A. Lane.

J. Opt. Soc. Amer., Vol. 56, No. 10, 1398-9 (Oct. 1966).

# 25800 VIBRATIONAL SPECTRA OF SPCl<sub>3</sub>, SPCl<sub>2</sub>F, SPClF<sub>2</sub>, AND SPF<sub>3</sub>.

J. R. Durig and J. W. Clark.

J. Chem. Phys. (USA), Vol. 46, No. 8, 3057-61 (15 April 1967).

The infrared spectra of thiophosphoryl trichloride and thiophosphoryl dichlorofluoride in both the liquid and gaseous states, and thiophosphoryl chlorodifluoride and thiophosphoryl trifluoride in only the gaseous state have been recorded from 4000 to 100 cm<sup>-1</sup>. The Raman spectra have also been recorded for the four thiophosphoryl trihalides in the liquid state and depolarization values measured. Complete vibrational assignments based on band contour positions, and depolarization values are given. The spectra are interpreted in detail assuming C<sub>s</sub> symmetry for thiophosphoryl dichlorofluoride and thiophosphoryl dichlorodifluoride and thiophosphoryl chlorodifluoride, and C<sub>3v</sub> symmetry for the other two molecules. The vibrational assignment proposed for the SPF<sub>3</sub> molecule is in marked contrast to that currently accepted. The P-S stretching vibration is found to decrease in frequency with the increased number of fluoride atoms attached to the phosphorous atom. Possible reasons for the decrease in frequency are discussed.

# 21685 EFFECTS OF TEMPERATURE ON THE NEAR-INFRARED ABSORPTION SPECTRA OF MOLECULES IN THE CONDENSED STATES. I. CARBON DIOXIDE.

W. C. Waggener, A. J. Weinberger and R. W. Stoughton.

J. Phys. Chem. (USA), Vol. 71, No. 13, 4320-5 (Dec. 1967).

The principal features of the absorption spectrum of liquid CO<sub>2</sub> in the region from 1.2 to 2.5  $\mu$  have been identified. The temperature dependence of the spectrum between 1.19 and 1.66  $\mu$  has been measured—in a frozen sample at -80° and 0.9 atm and at the triple point, -56.6° and 5.1 atm, in the liquid from the triple point to the critical point 31.1° and 72.9 atm, and in the gas from the critical point to 65° and 136 atm. The bands in liquid CO<sub>2</sub> at the triple point have  $\Delta\nu_{1/2} = 10-22$  cm<sup>-1</sup>, but broaden considerably with increasing temperature, viz., 25-75% at 0° and 200-400% at 65°. Freezing both increases the band heights and decreases the band widths by at least a factor of 2. The 1.6- $\mu$  bands have Lorentz profiles over the entire fluid range studied. Their composite intensity at the triple point (0.232 l. mole<sup>-1</sup> cm<sup>-2</sup>) increases nonlinearly with increasing temperature and with decreasing density, the latter parameter being by far the predominant one. The increase in intensity from the triple-point value is 6% at 2° and 16% at 25° in the liquid, and 380% in going to the dilute gas state at 25°. This dependence of the intensity upon density is in line with the Lorentz theory of band broadening of nonassociated molecules.



**22993** OBSERVATION OF THE SPECTRUM AND THE AMPLITUDE FLUCTUATIONS OF LIGHT PROPAGATING THROUGH NONEQUILIBRIUM LIQUID HELIUM. M. Iannuzzi. *Nuovo Cimento (Italy)*, Vol. 55, No. 2, 413-18 (11 June 1968).

The experimental results show that the spatial correlation function of the refractive index fluctuations in the liquid is adequately approximated by a Gaussian. Both the laser light scattered under a  $90^\circ$  angle and the amplitude fluctuations of light propagated through the liquid have been measured at the  $\lambda$ -point. No excess scattering at  $90^\circ$  and no anomalous amplitude fluctuations have been observed, in agreement with the information obtained by Lawson and Meyer (1954).

**23505** The infrared spectrum of liquid tetrafluorohydrazine. D.F. Koster, F.A. Miller (Mellon Inst., Pittsburgh, Pa., USA).

*Spectrochim. Acta (GB)*, vol.24A, no.9, p.1487-93 (Sept. 1968).

The infrared spectrum of liquid  $N_2F_4$  at  $-120^\circ C$  has been obtained and found to be essentially identical to that of the solid and the vapor. A comparison of these data with recent Raman results on the liquid indicates that a number of frequencies are mutually exclusive in the infrared and Raman spectra. This is taken as evidence for the presence of the *trans* isomer in addition to the *gauche* one. Their energies seem to be approximately equal. A vibrational assignment is suggested for both forms. (18 refs.)

**13529** Vibrational dynamics in liquid water: A new interpretation of the infrared spectrum of the liquid. J. Schuster (Dept. Chemistry, Temple Univ., Philadelphia, Pa., USA), D.E. Horng (Office of Sci. and Technology, White House, Washington, D.C., USA).

*J. Chem. Phys. (USA)*, vol.49, no.9, p.4150-50 (1 Nov. 1968).

In comparing the infrared spectra of liquid water and simple hydrates, two anomalies are noted which are apparently inexplicable in terms of presently acceptable theories of the liquid. These anomalies are explained in terms of a Maxwellian distribution of collisional interactions between water molecules which when put in quantitative form reveals (1) that most molecules in the liquid are highly distorted by collisional perturbations, and (2) that there is a broad distribution of distortion among the molecules in the liquid. When translated into vibrational dynamics these concepts lead to a continuum distribution of  $\nu_1$  and  $\nu_2$  modes of varying distorted molecules. It is shown that in its stretching motion, liquid water behaves dynamically as a continuum of O-H bond oscillators of different frequencies, demonstrating both weak inter- and intramolecular vibrational interactions. A new interpretation of the infrared spectrum of liquid water is given in terms of this model, and other spectral evidence is offered in support of it. (23 refs.)

**46641** Infra-red absorption spectrum for liquid ozone. A. Barbe, P. Jouve. *C.R. Acad. Sci. B (France)*, vol.268, no.26, p.1723-6 (30 June 1969). In French.

The authors report the first recording of the infra red spectrum for liquid ozone in liquid argon; between 400 and  $4700\text{ cm}^{-1}$ . Twenty one bands were observed and identified. Anharmonicity coefficients were determined with normal frequencies, allowing recalculation of the bounds observed; experimental and calculated values are in excellent agreement.

**22954** Far infrared absorption in liquid hydrogen. M.C. Jones (Nat. Bur. Standards, Boulder, Colo., USA).

*J. Chem. Phys. (USA)*, vol.51, no.9, p.3833-4 (1 Nov. 1969).

The far infrared spectra of liquid hydrogen at three para concentrations have been recorded in the wave number range 20 to  $250\text{ cm}^{-1}$ . The observed variation of the absorption coefficient with composition is consistent with the theory of translational absorption of Poll and Van Kranendonk (1961). (10 refs.)

**43458** Dispersion and absorption of liquid water in the infrared and radio regions of the spectrum. V.M. Zolotarev, B.A. Mikhailov, L.I. Alperovich, S.I. Popov.

*Optika i Spektrosk. (USSR)*, vol.27, no.5, p.790-4 (Nov. 1969). In Russian. English translation in: *Optics And Spectrosc. (USA)*, vol.27, no.5, p.430-2 (Nov. 1969).

The optical constants of liquid water in a broad spectral region ( $1\text{--}10^6\text{ }\mu\text{m}$ ) were determined by using four independent methods: transmission, reflection, DTR, and Kramer-Kronig. (21 refs.)

**27147** Far-infrared spectra of gaseous and liquid  $SF_6$ . A. Rosenberg, G. Birnbaum (North American Rockwell Corp., Thousand Oaks, Calif., USA).

*J. Chem. Phys. (USA)*, vol. 52, no. 2, p.683-6 (15 Jan. 1970).

The far infrared absorption spectrum of  $SF_6$  in the gaseous state was measured at  $25^\circ C$  at pressures from 3 to 19 atm in the wavelength region  $12\text{--}250\text{ }\mu\text{m}$ . The absorption of liquid  $SF_6$  in this region was measured at  $-40^\circ C$ . The strongest bands in the gas phase are centered roughly at  $50\text{ cm}^{-1}$ , and approximately at 94 and  $173\text{ cm}^{-1}$ . Bands centered at approximately 55, 90, and  $150\text{ cm}^{-1}$  were observed in the liquid.

**68110** Infrared spectra of liquid H<sub>2</sub>O and D<sub>2</sub>O. O.D.Bonner, J.D.Curry (Univ. South Carolina, Columbia, USA). *Infrared Phys. (GB)*, vol.10, no.2, p.91-4 (June 1970). Infrared spectra are reported for liquid H<sub>2</sub>O and D<sub>2</sub>O using a differential technique. This technique gives sharper bands whose positions are determined with greater certainty than those reported earlier in the literature. Frequency shifts upon liquefaction give evidence for greater association in H<sub>2</sub>O than in D<sub>2</sub>O. (12 refs.)

**18531** The near-infrared spectra of water and heavy water at temperatures between 25 and 390°. J.T.Bell, N.A.Krohn (Oak Ridge Nat. Lab., Tenn., USA).

*J. Phys. Chem. (USA)*, vol.74, no.22, p.4006 (29 Oct. 1970).

**18532** Comments on 'Near-infrared spectra of water and heavy water,' by Bell and Krohn. W.A.P.Luck.

*J. Phys. Chem. (USA)*, vol.74, no.22, p.4006-7 (29 Oct. 1970).

See ibid., vol.74, p.4006 (29 Oct 1970). (10 refs.)

**40002** Temperature dependence of the 1555 cm<sup>-1</sup> infrared absorption band in liquid D<sub>2</sub>O: inflection points. R.Oder, D.A.L.Goring (Pulp & Paper Res. Inst. Canada).

*Can. J. Chem. (Canada)*, vol.48, no.24, p.3793-6 (15 Dec. 1970).

The temperature dependence curves of the peak height, frequency, and half width of the infrared intermolecular combination band absorbing at 1555 cm<sup>-1</sup> in liquid D<sub>2</sub>O has been observed to behave sigmoidally between 5 and 70°C. No evidence of sharp discontinuities has been obtained but inflection points in the rather broad temperature interval of about 25 to 40°C have been observed. Results are discussed in terms of structural changes occurring in the liquid. (37 refs.)

**55616** Far infrared absorption in liquefied gases. M.C.Jones.

Report TN-390, Nat. Bur. Stand., Washington, D.C., USA (1970), 39 pp.

Experimental results are given for the absorption coefficient of the liquids hydrogen (three para concentrations), nitrogen, oxygen, carbon monoxide, methane and argon in the wavenumber range 20-250 cm<sup>-1</sup> (40-500 μm). In addition, data for liquid hydrogen are given at wave numbers up to 600 cm<sup>-1</sup> (16.7 μm). The results are discussed in terms of the induced dipole, and, in the case of carbon monoxide, the permanent dipole. An indication of the way in which the data may be employed in calculations of thermal radiative transfer is made by calculation of the modified Planck mean absorption coefficient.

**76076** Lambert absorption coefficients of water in the infrared.

C.W.Robertson, D.Williams (Kansas State Univ., Manhattan, USA).

*J. Opt. Soc. Am. (USA)*, vol.61, no.10, p.1316-20 (Oct. 1971).

By use of a wedge-shaped cell providing an absorbing layer tapering in thickness from less than one wavelength of visible light at one end to approximately 20 μm at the other end, the Lambert absorption coefficient for water has been measured in the spectral region between 4000 and 288 cm<sup>-1</sup>. After proper initial alignment of the cell windows had been established by the observation of interference fringes in the visible, film thicknesses at various positions along the wedge were measured by interferometric methods, employing convenient wavelengths in the infrared. The results of the study are presented in graphical and tabular form.

**67834** Influence of the effective field of a light wave on the observed spectrum of liquid water in the 4000-0.01-cm<sup>-1</sup> range. B.A.Mikhailov.

*Opt. & Spektrosk. (USSR)*, vol.32, no.1, p.227-30 (Jan. 1972). In Russian.

English translation in: *Opt. & Spectrosc. (USA)*, vol.32, no.1, p.120-1.

The author calculates the influence of the effective field of a light wave on the spectrum of liquid water over a wide spectral range, i.e., on absorption bands differing in both character and optical parameters. The feasibility of such a calculation became apparent after the calculation of the optical constants n and K of liquid water over a wide region of the spectrum 1 to 10<sup>6</sup> μm. (6 refs.)

**36004** Infrared absorption spectra of liquid and crystalline phases of thiophene. F.Tranchant, R.Guerin (Univ. Poitiers, Vienne, France).

*C.R. Hebd. Seances Acad. Sci. B (France)*, vol.274 no.12, p.795-8 (20 March 1972). In French.

The authors studied and compared the infrared absorption spectra of four crystalline phases of thiophene with that from the liquid phase. The crystal structure of the low temperature phase is obtained from the spectroscopic data. (10 refs.)

**57351** Infrared spectra of liquid and crystalline HCN and DCN.

M.Perolet, R.Savoye (Univ. Laval, Quebec, Canada).

*Can. J. Spectrosc. (Canada)*, vol.17, no.2, p.39-44 (March 1972).

The infrared spectra of liquid and solid HCN and DCN have been recorded. Reflection spectra were also obtained for the solids in both crystalline phases. The longitudinal frequencies were determined for all fundamental vibrations of the solids and the dipole derivatives associated with these transitions were calculated. (26 refs.)

**50316 Near-infrared studies of the structure of water. III. Mixed solvent systems.** G.R. Choppin, M.R. Violante (Florida State Univ., Tallahassee, USA). *J. Chem. Phys. (USA)*, vol. 56, no. 12, p. 5890-8 (15 June 1972). For pt. II see abstr. A154 of 1964. The near infrared absorption of water in the  $7000\text{ cm}^{-1}$  region has been studied for pure water and solutions of water acetone and water dioxane between 0 and  $80^\circ\text{C}$ . The absorption was resolved into Gaussian components and the component bands were used to calculate the mole fraction of water species with 0, 1, and 2 of the hydrogen atoms involved in hydrogen bonding. The data do not agree with the presence of significant effects due to Fermi resonance. A model of water with three spectroscopically distinct species agrees with the analysis of the bands. (35 refs.)

**50365 The correspondence of fundamental and combination bands in the infrared spectra of liquid H<sub>2</sub>O and D<sub>2</sub>O.** O.D. Bonner (Univ. South Carolina, Columbia, USA).

*Infrared Phys. (GB)*, vol. 12, no. 2, p. 109-14 (June 1972).

The frequencies of the fundamental  $\nu_1$ ,  $\nu_2$  and  $\nu_3$  bands for unbonded liquid H<sub>2</sub>O and D<sub>2</sub>O have been calculated from the frequencies observed for the combination bands in the near infrared region. The positions of the centers of the broad bands due to the hydrogen bonded species have also been estimated. All calculated values have been compared with the observed spectra of liquid H<sub>2</sub>O and D<sub>2</sub>O. It is concluded that the  $\nu_2$  bands observed at  $1645\text{ cm}^{-1}$  for H<sub>2</sub>O and  $1210\text{ cm}^{-1}$  for D<sub>2</sub>O are due to the 'monomeric' species. This is confirmed by the temperature dependence of these bands. (18 refs.)

**61039 The infra-red spectrum of water.** C.W. Robertson, B. Curmisse, D. Williams (Kansas State Univ., Manhattan, USA).

*Mol. Phys. (GB)*, vol. 26, no. 1, p. 183-91 (July 1973).

The Lambert absorption coefficient of water has been measured in the far infra-red spectral region  $800$  to  $50\text{ cm}^{-1}$ . The results, along with earlier measurements in the near infra-red, provide values of the imaginary part  $k$  of the refractive index over the spectral range  $4400$  to  $50\text{ cm}^{-1}$ . Kramers-Kronig techniques have been used to obtain values of the corresponding real part  $n$  of the refractive index over this spectral range. The values of these constants provide a complete quantitative description of the optical properties of water in the infra-red. (14 refs.)

**62103 Thermo-optical technique for the measurement of absorption loss spectrum in liquids.** J. Stone (Bell Labs., Holmdel, N.J., USA).

*Appl. Opt. (USA)*, vol. 12, no. 8, p. 1828-30 (Aug. 1973).

A thermo-optical technique is described for measuring the absorptivity spectrum of liquids using incoherent light. This technique is an extension of one previously used to measure absorptivity using coherent light, which was therefore limited to specific laser wavelengths. Absorptivities as small as  $2 \times 10^{-5}\text{ cm}^{-1}$  have been measured with  $2-3\text{ mW}$  of optical power. The absorptivity spectrum of chlorobenzene is characterized by lines due to overtones of C-H vibration in the infrared with low loss valleys in between. Measurements of carbon tetrachloride showed no measurable absorptivity (i.e., less than  $2 \times 10^{-5}\text{ cm}^{-1}$ ) between  $5600\text{ Å}$  and  $10600\text{ Å}$ . (5 refs.)

#### **1191 A STUDY OF THE INFRARED SPECTRA OF LIQUID OXYGEN AND NITROGEN.**

M. O. Bulanin and Yu. V. Peterson.

*Optika i Spektrosk. (USSR)*, Vol. 16, No. 6, 987-91 (June 1964).

In Russian. English translation in: *Optics and Spectrosc. (USA)*,

Vol. 16, No. 6, 533-5 (June 1964).

The infrared absorption spectra of technical liquid oxygen and nitrogen have been obtained in the region  $3500-1200\text{ cm}^{-1}$ , and a complete interpretation of them is given. It is shown that solutions of acetylene in liquid oxygen have a complex structure, and possible explanations of the observed phenomena are examined.

#### **7777 FAR INFRA-RED ABSORPTION IN LIQUID NITROGEN.**

N. W. B. Stone and D. Williams.

*Molecular Phys. (GB)*, Vol. 10, No. 1, 85-6 (Nov. 1965).

The present study is concerned with the far infra-red spectrum of liquid nitrogen. In view of the observed width of the vibration bands of liquid nitrogen and oxygen and the Raman evidence of quantized rotation in liquid hydrogen, it was considered possible that liquid nitrogen and oxygen might exhibit rotational absorption in the far infra-red. The present work has shown that both liquid nitrogen and liquid oxygen absorb in the spectral region between  $30\text{ cm}^{-1}$  and  $200\text{ cm}^{-1}$ ; nitrogen absorbs more strongly than oxygen.

### Far Infrared Absorption in Liquefied Gases

M. C. JONES. Natl. Bur. Std. (U. S.) Tech. Note 390. U. S. Government Printing Office, Washington, D. C., 1970. Pp. 39 (20×26 cm), paperbound. Price 50 cents.

Far-infrared absorption coefficients of liquid hydrogen (at three different parahydrogen concentrations), nitrogen, oxygen, carbon monoxide, methane, and argon are given. The data were obtained for all the liquefied gases from 20 to 250  $\text{cm}^{-1}$  (40–500  $\mu\text{m}$ ). In addition, data for liquid hydrogen are given up to 600  $\text{cm}^{-1}$  (16.7  $\mu\text{m}$ ).

The observed behavior is discussed in terms of the induced dipoles (and the permanent dipole in the case of carbon monoxide). A way in which the data may be employed in the calculation of the modified Planck mean absorption coefficient is indicated, and its application to calculating thermal radiative transfer in the liquids.